PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C07D 207/36, 213/64, 231/28, 233/54, 239/36, A01N 43/36, 43/40, 43/50, 43/54, 43/56, C07C 381/00, C07D 207/34, 233/84, 233/88, 521/00

A1

(11) International Publication Number: **WO 94/21606**

(43) International Publication Date: 29 September 1994 (29.09.94)

(21) International Application Number: PCT/GB94/00612

(22) International Filing Date: 24 March 1994 (24.03.94)

(30) Priority Data:
9306184.4 25 March 1993 (25.03.93) GB

(71) Applicant *(for all designated States except US)*: ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: SALMON, Roger [GB/GB]; 38 Tawfield, Bracknell, Berkshire RG12 4YU (GB). PEARSON, David, Philip, John [GB/GB]; 8 Sutton Close, Maidenhead, Berkshire SL6 4RP (GB). PARRY, David, Rees [GB/GB]; 30 Lowther Road, Emmbrook, Wokingham, Berkshire RG11 1JD (GB). KOZAKIEWICZ, Anthony, Marian [GB/GB]; Flat 4, Froghall, Froghall Drive, Wokingham, Berkshire RG11 2LS (GB).

(74) Agents: RICKS, Michael, James et al.; ICI Group Patents Services Dept., Shire Park, P.O. Box 6, Bessemer Road, Welwyn Garden City, Hertfordshire AL7 1HD (GB).

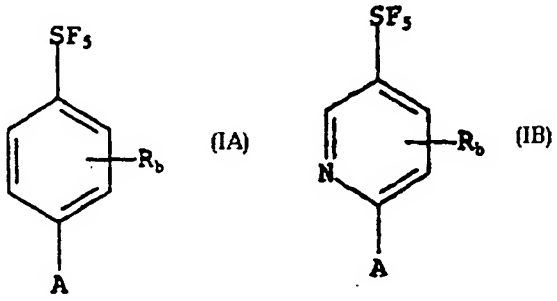
(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PENTAFLUOROSULPHANYLPHENYL AND PENTAFLUOROSULPHANYLPYRIDIL SUBSTITUTED HETEROAROMATIC COMPOUNDS WITH INSECTICIDAL OR ACARICIDAL ACTIVITY

(57) Abstract

Compounds with insecticidal or acaricidal activity have formula (IA) or (IB), wherein R_a represents hydrogen or from 1 to 4 optional substituents and R_b represents from 1 to 3 optional substituents and wherein A represents an optionally substituted N-linked nitrogen-containing five or six membered aromatic heterocyclic ring, for example imidazole, pyrrole, pyrazole, pyrimidinone and pyridone.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

Pentafluorosulphanylphenyl and Pentafluorosulphanylpyridil substituted heteroaromatic compounds with insecticidal or acaricidal activity

This invention relates to heteroaromatic compounds, and more particularly to phenyl-substituted heteroaromatic compounds to processes for their preparation and to their use as insecticides

According to the present invention there is provided a compound of formula (IA) or (IB) wherein R_a represents hydrogen or from 1 to 4 optional substituents and R_b represents from 1 to 3 optional substituents and wherein A represents an optionally substituted N-linked nitrogen-containing five or six membered aromatic heterocyclic ring, provided that when the compound is of formula (IA) and A represents a group of formula (IC) wherein $R^{1'}$ is hydrogen, halogen, or a group $NR^{4'}R^{5'}$ wherein $R^{4'}$ and $R^{5'}$ are independently selected from hydrogen or alkyl; $R^{2'}$ is a group $-S(O)_{n'}R^{6'}$ wherein n' is 0, 1 or 2 and $R^{6'}$ is a haloalkyl group; and $R^{3'}$ is -CN or is a group $CX'-NY^{1'}Y^{2'}$ wherein X' is O or S or S=O; and $Y^{1'}$ and $Y^{2'}$ are independently selected from hydrogen, nitro, amino or alkyl optionally substituted by halogen, by cycloalkyl, by formyl, by C_{2-7} alkanoyl, by C_{4-7} cycloalkylcarbonyl, by C_{2-7} alkoxycarbonyl, by C_{2-7} haloalkoxycarbonyl, by an aryl group or by an aromatic heterocyclic group or

$Y^{1'}$ and $Y^{2'}$ together with the nitrogen to which they are attached form an aliphatic heterocyclic group containing from 4 to 8 atoms in the ring and optionally substituted by halogen or alkyl or

$Y^{1'}$ and $Y^{2'}$ together form the group $=CHY^3$ wherein Y^3 is alkyl, C_{2-6} alkenyl, aryl, an aromatic heterocycle, or amino optionally substituted by alkyl or

$Y^{1'}$ is hydrogen and $Y^{2'}$ is alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl or a group $-S(O)_{n'}R^{6'}$ where $R^{6'}$ and n' are as hereinbefore defined, then R_a does not represent 2,6-dihalo.

According to a further aspect of the present invention there is provided a compound of formula (II) wherein X is $-CR^1=$ or -N=, R^1 and R^2 are independently selected from hydrogen, halogen, cyano, nitro, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkoxy, optionally substituted alkenyl or optionally substituted alkynyl or from a group $-S(O)_mR^5$ wherein m is 0, 1 or 2 and R^5 is optionally substituted alkyl or from a group $C(Y)-NR^6R^7$ where Y is =O or

=S and R^6 and R^7 are independently selected from hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or amino or R^6 and R^7 together with the nitrogen to which they are attached form an optionally substituted aliphatic heterocyclic ring containing from 4 to 8 atoms in the ring, or R^6 and R^7 together form the group $=CHR^{18}$ wherein R^{18} is optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, optionally substituted heterocyclyl or optionally substituted amino, or R^6 is hydrogen and R^7 is selected from alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl, or a group $-S(O)_mR^5$ as hereinbefore defined; and wherein R^3 and R^4 are independently selected from hydrogen, halogen, optionally substituted alkyl and optionally substituted cycloalkyl; and wherein A is as hereinbefore defined, provided that when X is $-CR^1$ and A represents a group of formula (IC) wherein $R^{1'}$ is hydrogen, halogen, or a group $NR^{4'}R^{5'}$ wherein $R^{4'}$ and $R^{5'}$ are independently selected from hydrogen or alkyl; $R^{2'}$ is a group $-S(O)_{n'}R^{6'}$ wherein n' is 0, 1 or 2 and $R^{6'}$ is a haloalkyl group; and $R^{3'}$ is -CN or is a group $CX'-NY^{1'}Y^{2'}$ wherein X' is O or S or S=O; and $Y^{1'}$ and $Y^{2'}$ are independently selected from hydrogen, nitro, amino or alkyl optionally substituted by halogen, by cycloalkyl, by formyl, by C_{2-7} alkanoyl, by C_{4-7} cycloalkylcarbonyl, by C_{2-7} alkoxycarbonyl, by C_{2-7} haloalkoxycarbonyl, by an aryl group or by an aromatic heterocyclic group or

$Y^{1'}$ and $Y^{2'}$ together with the nitrogen to which they are attached form an aliphatic heterocyclic group containing from 4 to 8 atoms in the ring and optionally substituted by halogen or alkyl or

$Y^{1'}$ and $Y^{2'}$ together form the group $=CHY^3$ wherein Y^3 is alkyl, C_{2-6} alkenyl, aryl, an aromatic heterocycle, or amino optionally substituted by alkyl or

$Y^{1'}$ is hydrogen and $Y^{2'}$ is alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl or a group $-S(O)_{n'}R^{6'}$ where $R^{6'}$ and n' are as hereinbefore defined, then R^1 and R^2 do not both represent halo.

Optional substituents which may be present in the aromatic heterocyclic group A may be independently selected for example from one or more of optionally substituted alkyl, optionally substituted cycloalkyl, halogen, cyano, nitro, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted

alkeneoxy, optionally substituted alkyneoxy, optionally substituted aralkyl, optionally substituted aryl, a group $-S(O)_mR^5$ as hereinbefore defined, a group $-NR^{11}R^{12}$ as hereinbefore defined, a group $-C(Y)-NR^6R^7$ as hereinbefore defined, a group $-N=CR^{16}R^{17}$ as hereinafter defined.

The term "alkyl" as used herein, including when present as a moiety in another group such as for example alkoxy, includes branched or straight chain alkyl, preferably containing from 1 to 6, and especially from 1 to 4 carbon atoms.

Optional substituents which may be present when the term "optionally substituted alkyl" is used include for example halogen, C_{3-7} cycloalkyl, alkoxy, thioalkyl, haloalkoxy, alkoxycarbonyl, hydroxy, cyano, nitro, optionally substituted aryl, optionally substituted amino. The alkyl moiety present in the above groups or other groups may be similarly substituted.

The term "optionally substituted amino" as used herein includes a group $-NR^{11}R^{12}$ wherein wherein R^{11} and R^{12} are independently selected from hydrogen, optionally substituted alkyl, alkoxycarbonyl, acyl, alkylthio-thiocarbonyl, alkylaminocarbonyl, aminocarbonyl or R^{11} and R^{12}, together with the nitrogen atom joining them, form a saturated or unsaturated C_{5-8} heterocyclic ring.

The term "alkenyl" as used herein includes branched or straight chain alkenyl, preferably containing from 2 to 6, and especially from 2 to 4 carbon atoms. Optional substituents which may be present in optionally substituted alkenyl groups include those mentioned above for alkyl.

The term "alkynyl" as used herein includes branched or straight chain alkynyl, preferably containing from 2 to 6, and especially from 2 to 4 carbon atoms. Optional substituents which may be present in optionally substituted alkenyl groups include those mentioned above for alkyl.

The term "aryl" as used herein includes phenyl and naphthyl optionally substituted with up to five substituents which may be independently selected from halogen, optionally substituted alkyl, optionally substituted alkoxy, hydroxy, cyano, nitro, optionally substituted amino, alkoxy carbonyl or a group $-S(O)_mR^5$ as hereinbefore defined. The term "aralkyl" indicates an alkyl group substituted by aryl. Optional substitution present in an aralkyl group may be present in either the alkyl or the aryl moiety or both.

The term heterocyclyl as used herein includes aromatic or non-aromatic single or fused rings comprising up to four heteroatoms in the rings selected from oxygen, nitrogen and sulphur and optionally substituted with aryl or with those substituents mentioned above as suitable for aryl.

It is preferred that R^3 and R^4 are both hydrogen.

It is preferred that X is a group $-C(R_1)=$.

Preferably R^1 (if present) and R^2 are independently selected from halogen, cyano and the group $C(Y)-NR^6R^7$. Preferably, R^1 (if present) is halogen, for example chloro, and R^2 is selected from halogen, for example chloro, cyano and the group $-C(Y)-NR^6R^7$.

When the group $-C(Y)-NR^6R^7$ is present as a substituent in a compound of the present invention, it is generally preferred that Y is =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4}alkyl.

When the group $-S(O)_mR^5$ is present as a substituent in a compound of the present invention, R^5 is preferably unsubstituted C_{1-4}alkyl or C_{1-4}haloalkyl. Suitable haloalkyl groups include fluoroalkyl or chlorofluoroalkyl groups, for example trifluoromethyl, pentafluoroethyl, chlorodifluoromethyl, dichlorofluoromethyl or difluoroethyl such as 1,1-difluoroethyl.

When an optionally substituted amino group $-NR^{11}R^{12}$ is present as a substituent in a compound of the present invention it is generally preferred that R^{11} and R^{12} are independently selected from hydrogen and C_{1-4}alkyl.

Preferably A is is optionally substituted N-linked imidazole, optionally substituted N-linked pyrrole, optionally substitued N-linked pyrimidinone or optionally substituted N-linked pyridone.

Compounds of the invention wherein A represents optionally substituted N-linked imidazole preferably have the structure (III) wherein X, R^2, R^3 and R^4 have the meanings given previously; R^8 represents hydrogen, optionally substituted alkyl, halogen, optionally substituted alkoxy, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aralkyl or a grup $-S(O)_mR^5$ as hereinbefore defined; R^9 represents hydrogen or optionally substituted alkyl, for example haloalkyl, or a group $-S(O)_mR^5$ wherein m and R^5 are as defined previously; and R^{10} represents hydrogen or a group $-S(O)_mR^5$ as hereinbefore defined or $-NR^1{}_1R^{12}$ as hereinbefore defined.

If R^1 or R^2 is cyano or a group $-C(Y)-NR^6R^7$ and R^{10} is a group $-NR^{11}R^{12}$ wherein at least one of R^{11} or R^{12} is hydrogen, internal cyclisation may take place between the groups R^1 (or R^2) and R^{10}. It is preferred therefore that if R^1 or R^2 is cyano or a group $-C(Y)-NR^6R^7$, and R^{10} is a group $-NR^{11}R^{12}$ then both R^{11} and R^{12} are alkyl.

It is preferred that R^8 is hydrogen, alkyl or halogen.

It is preferred that R^9 is hydrogen, haloalkyl or a group $-S(O)_mR^5$ wherein m is 0, 1 or 2 and R^5 is haloalkyl. When R^9 and R^5 are haloalkyl, they are preferably fluoroalkyl or fluorochloroalkyl, for example trifluoromethyl or pentafluoroethyl.

It is preferred that R^{10} is hydrogen or a group $-NR^{11}R^{12}$ wherein R^{11} and R^{12} are independently selected from hydrogen and alkyl.

It is preferred that at least one of R^8, R^9 and R^{10} is other than hydrogen.

Thus according to a further aspect of the present invention there is provided a compound of formula (III) wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;R^3 and R^4 are hydrogen; R^8 is hydrogen, C_{1-4} alkyl optionally substitued by halogen, halogen, or a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen; R^9 is hydrogen or C_{1-4} alkyl optionally substituted by halogen, or a group $-S(O)_mR^5$ as herein defined; and R^{10} represents hydrogen or $-NR^{1}_{1}R^{12}$ wherein R^{11} and R^{12} are are independently selected from hydrogen and C_{1-4} alkyl.

Compounds of the invention wherein A represents optionally substituted N-linked pyrazole preferably have the structure (IV) wherein X, R^2, R^3 and R^4 have the meanings given previously; and wherein R^{13} is cyano or a group $-C(Y)-NR^6R^7$ as hereinbefore defined; R^{14} is a group $-S(O)_mR^5$ as hereinbefore defined; and R^{15} is hydrogen, halogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted alkeneoxy, optionally substituted alkyneoxy, optionally substituted aryl, a group $-S(O)_mR^5$ as hereinbefore defined, a group $-NR^{11}R^{12}$ as hereinbefore defined or a group $-N=CR^{16}R^{17}$ wherein R^{16} and R^{17} are independently selected from hydrogen, optionally substituted alkyl, optionally substituted alkoxy, a group $-S(O)_mR^5$ as hereinbefore defined, a group $-NR^{11}R^{12}$ as hereinbefore defined,

optionally substituted aryl, optionally substituted aromatic heterocyclyl, or R^{16} and R^{17} together with the carbon atom joining them form a $_{5-8}$ saturated or unsaturated carbocyclic ring or heterocyclic ring, provided that when X is $-CR^1$ and A represents a group of formula (IC) wherein $R^{1'}$ is hydrogen, halogen, or a group $NR^{4'}R^{5'}$ wherein $R^{4'}$ and $R^{5'}$ are independently selected from hydrogen or alkyl; $R^{2'}$ is a group $-S(O)_{n'}R^{6'}$ wherein n' is 0, 1 or 2 and $R^{6'}$ is a haloalkyl group; and $R^{3'}$ is -CN or is a group $CX'-NY^{1'}Y^{2'}$ wherein X' is O or S or S=O; and $Y^{1'}$ and $Y^{2'}$ are independently selected from hydrogen, nitro, amino or alkyl optionally substituted by halogen, by cycloalkyl, by formyl, by C_{2-7} alkanoyl, by C_{4-7} cycloalkylcarbonyl, by C_{2-7} alkoxycarbonyl, by C_{2-7} haloalkoxycarbonyl, by an aryl group or by an aromatic heterocyclic group or

$Y^{1'}$ and $Y^{2'}$ together with the nitrogen to which they are attached form an aliphatic heterocyclic group containing from 4 to 8 atoms in the ring and optionally substituted by halogen or alkyl or

$Y^{1'}$ and $Y^{2'}$ together form the group $=CHY^3$ wherein Y^3 is alkyl, C_{2-6} alkenyl, aryl, an aromatic heterocycle, or amino optionally substituted by alkyl or

$Y^{1'}$ is hydrogen and $Y^{2'}$ is alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl or a group $-S(O)_{n'}R^{6'}$ where $R^{6'}$ and n' are as hereinbefore defined, then R^1 and R^2 do not both represent halo.

Alternatively, compounds of the invention wherein A represents optionally substituted N-linked pyrazole may have a structure (IV) wherein X, R^2, R^3 and R^4 have the meanings given previously, R^{13} and R^{14} are as defined above and R^{15} is optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted alkeneoxy, optionally substituted alkyneoxy, optionally substituted aryl, a group $-S(O)_mR^5$ as hereinbefore defined, or a group $-N=CR^{16}R^{17}$ wherein R^{16} and R^{17} are independently selected from hydrogen, optionally substituted alkyl, optionally substituted alkoxy, a group $-S(O)_mR^5$ as hereinbefore defined, a group $-NR^{11}R^{12}$ as hereinbefore defined, optionally substituted aryl, optionally substituted aromatic heterocyclyl, or R^{16} and R^{17} together with the carbon atom joining them form a $_{5-8}$ saturated or unsaturated carbocyclic ring or heterocyclic ring.

Preferably R^{13} is cyano.

Preferably R^{14} is a group $-S(O)_mR^5$ wherein m is 0, 1 or 2 and R^5 is haloalkyl, and especially fluoroalkyl such as trifluoromethyl or pentafluoroethyl or chlorofluoroalkyl.

Preferably R^{15} is alkoxy or thioalkyl (a group $-S(O)_mR^5$ wherein m is 0 and R^5 is alkyl) or is a group $-N=CR^{16}R^{17}$ wherein R^{16} is alkyl or hydrogen and R^{17} is optionally substituted alkyl, for example alkyl optionally substituted with alkoxy, or is optionally substituted phenyl, for example phenyl substituted by hydroxy and optionally one or more groups, for example alkoxy.

Thus according to a further aspect of the present invention there is provided a compound of formula (IV) wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, and R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; R^3 and R^4 are hydrogen; R^{13} is cyano or a group $-C(Y)-NR^6R^7$ as herein defined; R^{14} is a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen; and R^{15} is C_{1-4} alkoxy, or a group $-S(O)_mR^5$ as herein defined.

Compounds of the invention wherein A represents optionally substituted N-linked pyrrole preferably have the structure (V) wherein X, R^2, R^3 and R^4 have the meanings given previously; and wherein R^{19} represents hydrogen, halogen, a group $-S(O)_mR^5$ as hereinbefore defined, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted alkeneoxy, optionally substituted alkyneoxy, a group $-NR^{11}R^{12}$ as defined herein or a group $-N=CR^{16}R^{17}$ as defined herein; R^{20} represents hydrogen, a group $-S(O)_mR^5$ as hereinbefore defined, optionally substituted alkyl, optionally substituted alkenyl or optionally substituted alkynyl; R^{21} represents cyano or a group $-C(Y)-NR^6R^7$ as hereinbefore defined; and R^{22} represents hydrogen, halogen, a group $-S(O)_mR^5$ as hereinbefore defined, optionally substituted alkyl optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted alkoxy, optionally substituted alkeneoxy or optionally substituted alkyneoxy.

If R^1 or R^2 is cyano or a group $-C(Y)-NR^6R^7$ and R^{19} is a group $-NR^{11}R^{12}$ wherein at least one of R^{11} or R^{12} is hydrogen, internal cyclisation may take place between the groups R^1 (or R^2) and R^{19} (or R^{22}).

It is preferred therefore that if R^1 or R^2 is cyano or a group $-C(Y)-NR^6R^7$, and R^{19} or R^{22} is a group $-NR^{11}R^{12}$ then both R^{11} and R^{12} are alkyl.

Preferably R^{19} represents, hydrogen, halogen, a group $-NR^{11}R^{12}$ wherein R^{11} and R^{12} independently represent hydrogen or alkyl and preferably both represent hydrogen, or a group $-S(O)_mR5$ wherein m is 0 and R^5 is alkyl.

Preferably R20 represents a group $-S(O)_mR^5$ wherein m is 0, 1 or 2 and R^5 is haloalkyl, for example fluoroalkyl or chlorofluoroalkyl. As specific examples of such groups there may be mentioned trifluoromethyl, pentafluoroethyl, dichlorofluoromethyl and chlorodifluoromethyl.

Preferably R^{21} represents cyano.

Preferably, R^{22} represents hydrogen, halogen, for example chloro, or a group $-S(O)_mR^5$ wherein R^5 is haloalkyl, for example trifluoroalkyl or pentafluoroethyl.

Thus according to a further aspect of the present invention there is provided a compound of formula (V) wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; R^3 and R^4 are hydrogen; and wherein R^{19} represents hydrogen, halogen, a group $-NR^{11}R^{12}$ wherein R^{11} and R^{12} independently represent hydrogen of C_{1-4} alkyl or a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen; R^{20} is hydrogen or a group $-S(O)_mR^5$ as herein defined, R^{21} represents cyano or a group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; and R^{22} represents hydrogen, halogen, a group $-S(O)_mR^5$ as herein defined.

Compounds of the invention wherein A represents optionally substituted N-linked pyrimidinone preferably have the structure (VI) wherein X, R^2, R^3 and R^4 have the meanings given previously; R^{23} is oxygen or sulphur; R^{24} is hydrogen, halogen, $-NR^{11}R^{12}$ as hereinbefore defined, $-S(O)_mR^5$ as hereinbefore defined, alkyl or cycloalkyl; R^{25} is halogen, nitro, haloalkyl, haloalkoxy or $-S(O)_mR^5$ as hereinbefore defined; and R^{26} is hydrogen, optionally substituted alkyl, halogen, cyano, alkoxy, $-S(O)_mR^5$ as hereinbefore defined, , $NR^{11}R^{12}$ as hereinbefore defined, formyl or nitro.

Preferably R^{23} is oxygen.

Preferably R^{24} is hydrogen.

Preferably R^{25} is fluoroalkyl, for example trifluoromethyl or pentafluoroethyl.

Preferably R^{26} is hydrogen or alkyl.

Thus according to a further aspect of the present invention there is provided a compound of formula (VI) wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; R^3 and R^4 are hydrogen; R^{23} is oxygen or sulphur; R^{24} is hydrogen, R^{25} is C_{1-4} haloalkyl; and R^{26} is hydrogen or C_{1-4} alkyl.

Compounds of the invention wherein A represents optionally substituted N-linked pyridone preferably have the structure (VII) wherein X, R^2, R^3 and R^4 have the meanings given previously; R^{27} is oxygen or sulphur, R^{28} is hydrogen, halogen, a group $-NR^{11}R^{12}$ as hereinbefore defined, optionally substituted alkyl, for example haloalkyl, optionally substituted alkoxy, for example haloalkoxy and optionally substituted thioalkyl, for example halothioalkyl; R^{29} is hydrogen, halogen, a group $-NR^{11}R^{12}$ as hereinbefore defined, optionally substituted alkyl, for example haloalkyl, optionally substituted alkoxy, for example haloalkoxy and optionally substituted thioalkyl, for example halothioalkyl, cyano, nitro, optionally substituted oximino, optionally substituted alkenyl, optionally substituted aryloxy, or a group $-S(O)_mR^5$ as hereinbefore defined; R30 is hydrogen, optionally substituted alkyl, for example haloalkyl, alkenyl optionally substituted by halogen or by a group $-COOR^{32}$ wherein R^{32} is alkyl optionally substituted by halogen; and R^{31} is a group R^{28} as defined above or a cyano or nitro group.

Preferably R^{27} is oxygen.

Preferably R^{28} is hydrogen.

Preferably R^{29} is hydrogen, halogen or haloalkyl, for example fluoroalkyl such as trifluoromethyl or pentafluoroethyl.

Preferably R^{30} is hydrogen or haloalkyl.

Preferably R^{31} is hydrogen, halogen, nitro or cyano.

Thus according to a further aspect of the present invention there is provided a compound of formula (VII) wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; R^3 and R^4 are hydrogen; R^{28} is hydrogen; R^{29} is hydrogen, halogen or C_{1-4} haloalkyl; R30 is hydrogen, or C_{1-4} haloalkyl; and R^{31} is hydrogen, halogen, nitro or cyano.

Examples of compounds of the present invention having the formula (III) wherein X is $-CR^1=$ are set out in Table I. Examples of compounds of the present invention having the formula (IV) are set out in Table II. Examples of compounds of the present invention having the formula (V) are set out in Table III. Examples of compounds of the present invention having the formula (VI) are set out in Table IV. Examples of compounds of the present invention having the formula (VII) are set out in Table V.

TABLE I

Compound Number	R^1	R^2	R^3	R^4	R^8	R^9	R^{10}
1	Cl	Cl	H	H	H	H	H
2	Cl	Cl	H	H	H	CF_3	H
3	Cl	Cl	H	H	CH_3	CF_3	H
4	Cl	Cl	H	H	CH_3	C_2F_5	H
5	Cl	CN	H	H	H	CF_3	H
6	Cl	Cl	H	H	H	SCF_3	NH_2
7	Cl	Cl	H	H	H	SCF_3	H
8	Cl	Cl	H	H	H	$SOCF_3$	H
9	Cl	Cl	H	H	H	SO_2CF_3	H
10	Cl	Cl	H	H	$SCFCl_2$	H	H
11	Cl	Cl	H	H	H	C_2F_5	H
12	Cl	Cl	H	H	Cl	SCF_3	NH_2
13	Cl	Cl	H	H	Cl	SCF_3	H
32	Cl	CN	H	H	H	C_2F_5	H
33	CN	Cl	H	H	CH_3	C_2F_5	H

TABLE II

Compound Number	R^1	R^2	R^3	R^4	R^{13}	R^{14}	R^{15}
14	Cl	Cl	H	H	CN	SCF_3	SCH_3
15	Cl	Cl	H	H	CN	SO_2CF_3	OCH_3
16	Cl	Cl	H	H	CN	SCF_3	CH_3
17	Cl	Cl	H	H	CN	SCF_3	(Strucure VIII)

TABLE III

Compound Number	R^1	R^2	R^3	R^4	R^{19}	R^{20}	R^{21}	R^{22}
18	Cl	Cl	H	H	NH_2	H	CN	H
19	Cl	Cl	H	H	NH_2	$SCCl_2F$	CN	H
20	Cl	Cl	H	H	NH_2	$SCCl_2F$	CN	Cl
21	Cl	Cl	H	H	NH_2	$SOCCl_2F$	CN	Cl
22	Cl	Cl	H	H	SCH_3	$SOCCl_2F$	CN	Cl
23	Cl	Cl	H	H	NH_2	SCF_3	CN	SCF_3
24	Cl	Cl	H	H	NH_2	SCF_3	CN	H
25	Cl	Cl	H	H	Br	$SCCl_2F$	CN	Cl
26	Cl	Cl	H	H	H	$SCCl_2F$	CN	Cl
27	Cl	Cl	H	H	NH_2	SCF_3	CN	Cl
28	Cl	Cl	H	H	SCH_3	SCF_3	CN	SCF_3

TABLE IV

Compound Number	R^1	R^2	R^3	R^4	R^{23}	R^{24}	R^{25}	R^{26}
29	Cl	Cl	H	H	O	H	CF_3	H
30	Cl	Cl	H	H	O	H	C_2F_5	H

TABLE V

Compound Number	R^1	R^2	R^3	R^4	R^{27}	R^{28}	R^{29}	R^{30}	R^{31}
31	Cl	Cl	H	H	O	H	CF_3	H	Cl

Compounds corresponding to each of the above compounds in Tables I to V wherein, in place of the values of R^1 and R^2 listed, R^1 is Cl and R^2 is

CN should also be considered as being specifically disclosed as should compounds wherein R^1 is Cl and R^2 is F.

In general, compounds of formula (IA), (IB) and (II) may be prepared by the reaction of Scheme I wherein AH is the appropriate heterocyclic compound carrying a hydrogen atom on the heterocyclic nitrogen and Z is a leaving group such as halogen, and especially chlorine or fluorine. Thus for example, when A is imidazole, the reaction of Scheme (1) is as more specifically illustrated is Scheme (2). The reaction suitably takes place in the presence of a base such as an alkali metal hydride, an alkali metal alkoxide or an alkali metal carbonate and in a suitable solvent. An especially suitable base is sodium hydride and the reaction suitably takes place under an inert atmosphere and in the presence of a polar aprotic solvent such as dimethylformamide or dimethylacetamide or N-methylpyrrolin-2-one. Other suitable solvents include hydrocarbon solvents such as petroleum ether or toluene or an alcohol or an ether such as tetrahydrofuran. The reaction temperature is conveniently in the range 0°C to 120°C, for example 20°C to 65°C.

In an alternative approach, the heterocyclic ring may be prepared by cyclisation. Such a cyclisation process for the imidazole ring is illustrated for example in Scheme 3 using a general method more specifically described in EP 0 396 427.

A similar cyclisation process is illustrated in Scheme 4 for the preparation of pyrazoles. A corresponding cyclisation process for the preparation of pyrroles is illustrated in Scheme 5 using a general method more specifically described in EP 0 460 940.

Scheme 2 illustrates a reaction in which the substituents R^1, R^2, R^3, R^4, R^8, R^9 and R^{10} are present in the starting materials. Those skilled in the art will appreciate that it is also possible for precursors to any of the groups R^1, R^2, R^3, R^4, R^8, R^9 and R^{10} to be present in the starting materials and for such groups to be converted to the groups R^1, R^2, R^3, R^4, R^8, R^9 or R^{10} after the reaction has taken place. Similarly, Schemes 3 to 5 have as their final product a specific compound of the invention which may then be converted to other compounds of the invention using appropriate conversion reactions. A number of appropriate conversion reactions are illustrated in the Examples. Other suitable conversion reactions are described in the art or will occur to those skilled in the art.

Compounds of formula (XII) may be prepared by the general method of Scheme 6 which illustrates the preparation of the compound of formula (XXII). Suitable chlorinating agents include N-chlorosuccinimide and concentrated hydrochloric acid in the presence of hydrogen peroxid. Compound (XX) may be prepared as described in the Journal of the Americal Chemical Society 84 3064 (1962).

Typical reactions for the preparation of specific compounds of general formula (IX) are illustrated in Schemes 7 and 8 and more specifically described in the Examples herein. Variants of such reactions suitable for the preparation of other compounds of general formula (IX) will occur to those skilled in the art.

Intermediate compounds of general formula (XIII) in Scheme 3, (XVII) in Scheme 4, (XIX) in Scheme 5, (XXIII) and (XXIV) in Scheme 7, (XXV) and (XXVI) in Scheme 8, and (XXVII) and (XXVIII) in Scheme 8 are believed to be novel and form a further aspect of the present invention. Intermediates wherein R^3 and R^4 are hydrogen are especially preferred. Further novel intermediate compounds are illustrated in the Examples and include for example 3,4,5-trichlorobenzenesulphurpentafluoride, 3,5-dichloro-benzenesulphurpentafluoride, 3,5-dichloro-4-fluorobenzenesulphurpenta-fluoride, 3-chloro-4,5-difluorobenzenesulphurpentafluoride, 4-amino-3-bromobenzenesulphurpentafluoride *, 4-amino-3-cyanobenzene-sulphurpentafluoride *, 4-amino-3-chloro-5-cyanobenzenesulphurpentafluoride * and 3-cyano-4,5-dichlorobenzenesulphurpentafluoride. Certain intermediates, and in particular those marked above with an asterisk (*) may have insecticidal activity in their own right.

The compounds of formula (I) may be used to combat and control infestations of insect pests and also other invertebrate pests, for example, acarine pests. The insect and acarine pests which may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, forestry, the storage of products of vegetable origin, such as fruit, grain and timber, and also those pests associated with the transmission of diseases of man and animals.

Thus according to a further aspect of the present invention there is provided an insecticidal or acaricidal composition comprising an

insecticidally or acaricidally effective amount of a compound according to the invention in association with an insecticidally or acaricidally inert dilutent or carrier.

In order to apply the compounds to the locus of the pests they are usually formulated into compositions which include in addition to the insecticidally active ingredient or ingredients of formula I suitable inert diluent or carrier materials, and/or surface active agents. The compositions may also comprise another pesticidal material, for example another insecticide or acaricide, or a fungicide, or may also comprise an insecticide synergist, such as for example dodecyl imidazole, safroxan, or piperonyl butoxide.

The compositions may be in the form of dusting powders wherein the active ingredient is mixed with a solid diluent or carrier, for example kaolin, bentonite, kieselguhr, or talc, or they may be in the form of granules, wherein the active ingredient is absorbed in a porous granular material for example pumice.

Alternatively the compositions may be in the form of baits wherein the active ingredient is mixed with a nutrient carrier for example sucrose, yeast, malt extract, cereal or cereal products and optionally an attractant such as a pheromone or pheromone analogue.

Alternatively the compositions may be in the form of liquid preparations to be used as dips or sprays, which are generally aqueous dispersions or emulsions of the active ingredient in the presence of one or more known wetting agents, dispersing agents or emulsifying agents (surface active agents).

Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic or non-ionic type. Suitable agents of the cationic type include, for example, quaternary ammonium compounds, for example cetyltrimethyl ammonium bromide. Suitable agents of the anionic type include, for example, soaps, salts of aliphatic monoesters of sulphuric acid, for example sodium lauryl sulphate, salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, or butylnaphthalene sulphonate, and a mixture of the sodium salts of diisopropyl- and triisopropylnaphthalene sulphonates. Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl

alcohol or cetyl alcohol, or with alkyl phenols such as octyl phenol, nonyl phenol and octyl cresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, and the lecithins.

The compositions may be prepared by dissolving the active ingredient in a suitable solvent, for example, a ketonic solvent such as diacetone alcohol, or an aromatic solvent such as trimethylbenzene and adding the mixture so obtained to water which may contain one or more known wetting, dispersing or emulsifying agents.

Other suitable organic solvents are dimethyl formamide, ethylene dichloride, isopropyl alcohol, propylene glycol and other glycols, diacetone alcohol, toluene, kerosene, white oil, methylnaphthalene, xylenes and trichloroethylene, N-methyl-2- pyrrolidone and tetrahydrofurfuryl alcohol (THFA).

The compositions which are to be used in the form of aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient or ingredients, the said concentrate to be diluted with water before use. These concentrates are often required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may contain 10-85% by weight of the active ingredient or ingredients. When diluted to form aqueous preparations such preparations may contain varying amounts of the active ingredient depending upon the purpose for which they are to be used. For agricultural or horticultural purposes, an aqueous preparation containing between 0.0001% and 0.1% by weight of the active ingredient (approximately equivalent to from 5-2000g/ha) is particularly useful.

In use the compositions are applied to the pests, to the locus of the pests, to the habitat of the pests, to growing plants liable to infestation by the pests, or, where there is systemic uptake by plants, to the soil surrounding plants liable to infestation, by any of the known means of applying pesticidal compositions, for example, by dusting or spraying.

Thus according to a further aspect of the present invention there is provided a method of combating insect and acarine pests at a locus which comprises treating the locus with an insecticidally or acaricidally effective amount of a composition according to the present invention.

The compounds of the invention may be the sole active ingredient of the composition or they may be admixed with one or more additional active ingredients such as insecticides, insecticide synergists, herbicides, fungicides or plant growth regulators where appropriate.
Suitable additional active ingredients for inclusion in admixture with the compounds of the invention may be compounds which will broaden the spectrum of activity of the compounds of the invention or increase their persistence in the location of the pest. They may synergise the activity of the compound of the invention or complement the activity for example by increasing the speed of effect, improving knockdown or overcoming repellency. Additionally multi-component mixtures of this type may help to overcome or prevent the development of resistance to individual components.

The particular insecticide, herbicide or fungicide included in the mixture will depend upon its intended utility and the type of complementary action required. Examples of suitable insecticides include the following:

a) Pyrethroids such as permethrin, esfenvalerate, deltamethrin, cyhalothrin in particular lambda-cyhalothrin, cypermethrin, alpha cypermethrin, bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids for example ethofenprox, natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin, or 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl-3-(2-oxothiolan--3-ylidenemethyl) cyclopropane carboxylate;

b) Organophosphates such as profenofos, sulprofos, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chloropyrifos, phosalone, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, fenitrothion or diazinon;

c) Carbamates (including aryl carbamates) such as pirimicarb, cloethocarb, carbofuran, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur or oxamyl;

d) Benzoyl ureas such as triflumuron, or chlorfluazuron;

e) Organic tin compounds such as cyhexatin, fenbutatin oxide, or

azocyclotin;

f) Macrolides such as avermectins or milbemycins, for example such as abamectin, ivermectin, and milbemycin;

g) Hormones such as pheromones;

h) Organochlorine compounds such as benzene hexachloride, DDT, chlordane or dieldrin.

i) Amidines, such as chlordimeform or amitraz.

In addition to the major chemical classes of insecticide listed above, other insecticides having particular targets may be employed in the mixture if appropriate for the intended utility of the mixture. For instance selective insecticides for particular crops, for example stemborer specific insecticides for use in rice such as cartap or buprofezin can be employed. Alternatively insecticides specific for particular insect species/stages for example ovo-larvicides such as clofentezine, flubenzimine, hexythiazox and tetradifon, acaricides such as dicofol, propargite, bromopropylate, chlorobenzilate, or growth regulators such as hydramethylnon, cyromazine, methoprene, hydroprene, chlorfluazuron and diflubenzuron may also be included in the compositions.

Examples of suitable insecticide synergists for use in the compositions include piperonyl butoxide, sesamex, and dodecyl imidazole.

Suitable herbicides, fungicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required. An example of a rice selective herbicide which can be included is propanil, an example of a plant growth regulator for use in cotton is "Pix", and examples of fungicides for use in rice include blasticides such as blasticidin-S.

The ratio of the compound of the invention to the other active ingredient in the composition will depend upon a number of factors including type of target, effect required from the mixture etc.

However in general, the additional active ingredient of the composition will be applied at about the rate as it is usually employed, or at a slightly lower rate if synergism occurs.

The compounds of the present invention and compositions comprising them have shown themselves active against a variety of insect and other invertebrate pests. Compounds of the present invention are also generally characterised by a relatively broad spectrum of activity which may include

Lepidoptera and Coleoptera in addition to public health pests such as flies and cockroaches.

The efficacy of certain insecticides against the target species, for example public health pests such as flies and cockroaches, may be reduced dramatically over a period of years as the target species develop resistance to the insecticide. Thus the presence of resistant strains of housefly and other public health pests in many parts of the world can be a serious problem and limits the use of insecticides such as lindane/dieldrin and more generally the general class of insecticides known as cyclodienes. Resistance can persist many years after an insecticide has ceased to be in widespread use and what is more, resistant strains of the target species may also prove to be resistant to novel insecticides. Such "cross-resistance" may mean that even a novel insecticide is effective only against susceptible strains of the target species and has relatively little effect on resistant strains. This can prove a serious limitation.

Thus compounds of the present invention may also be active against organophosphate, pyrethroid or cyclodiene (for example lindane or dieldrin) resistant strains of public and animal health pests. They may be effective in combating both susceptible and resistant strains of the pests in their adult and immature stages of growth, and may be applied to the infested host animal by topical, oral or parenteral administration.

The following Examples illustrate the invention. Throughout the Examples, the term 'ether' refers to diethyl ether, magnesium sulphate was used to dry solutions except where otherwise indicated, and solutions were concentrated under reduced pressure. All reactions were performed under an atmosphere of nitrogen and solvents were dried before use, where appropriate. Unless otherwise stated, chromatography was performed on a column of silica gel as the stationary phase. Where shown NMR and other data are selective; no attempt is made to list every absorption in all cases. ^{1}H NMR spectra were recorded using $CDCl_3$-solutions unless otherwise stated. The following abbreviations are used throughout:

NMR = nuclear magnetic resonance	ppm = parts per million
m = multiplet	s = singlet
d = doublet	melting points are in °C
mp = melting point	DMF = N,N-dimethylformamide

PREPARATION 1

Preparation of 4-aminobenzenesulphurpentafluoride

4-Nitrobenzenesulphurpentafluoride (26.7g) in propan-2-ol (220 cm^3) containing water (40 cm^3) and concentrated hydrochloric acid (3 cm^3) was treated with reduced iron powder (54g). The mixture was stirred and heated to reflux for 2 hours, cooled to 65° and neutralised with saturated aqueous potassium carbonate. The mixture was filtered whilst hot through a bed of keiselghur, and washed through with further propan-2-ol. The filtrate was evaporated under reduced pressure, the residual solid dissolved in diethyl ether (200 cm^3), filtered and the filtrate evaporated to give the required product as a fawn solid.

^1H NMR $\delta(CDCl_3)$ broad signal 4.0 (2H), 6.62(d,2H), 7.53(d,2H)

PREPARATION 2

Preparation of 3,5-dichloro-4-aminobenzenesulphurpentafluoride

4-Aminobenzenesulphurpentafluoride (20.0g) in dry acetonitrile (150 cm^3) was stirred at ambient temperature and treated with N-chlorosuccinimide (26.7g) in portions over 2 hours. The mixture was stirred for 18 hours, heated to reflux for 1¼ hour and evaporated under reduced pressure. The residue was partitioned between hexane (600 cm^3) and aqueous sodium bicarbonate. The hexane fraction was washed twice with water and dried (anhydrous magnesium sulphate) and evaporated under reduced pressure to give the required product as a pale brown solid.

^1H NMR $\delta(CDCl_3)$ 4.80(broad,2H), 7.60(s,2H).

PREPARATION 3

Preparation of 3,4,5-Trichlorobenzenesulphurpentafluoride

4-Amino-3,5-dichlorobenzenesulphurpentafluoride (5.76g) in dry acetonitrile (30 cm^3) was added dropwise to a stirred mixture of copper (II) chloride 3.23g) and tertiary butylnitrite (3.1g, 3.56 cm^3) in dry acetonitrile (50 cm^3) at 60-5° under an atmosphere of nitrogen. On complete addition the reaction was kept at 60-5° for 1 hour, cooled and poured into water (700 cm^3). The mixture was acidified with concentrated hydrochloric acid and extracted with hexane (2 x 250 cm^3). The hexane fractions were washed with water and dried (anhydrous magnesium sulphate). The solvent was evaporated under reduced pressure to give a brown liquid which was distilled at 120-130°/12mm Hg. to give a mixture of the required product (A) and 3,5-dichlorobenzenesulphurpentafluoride (B).

(A) ^{1}H NMR δ($CDCl_3$) 7.80(s), Molecular ion 306;
(B) ^{1}H NMR δ($CDCl_3$) 7.54(d,1H), 7.67(d,2H).

PREPARATION 4

Preparation of (A) 3,5-Dichloro-4-fluorobenzenesulphurpentafluoride and (B) 3-Chloro-4,5-difluorobenzenesulphurpentafluoride

The mixture from Preparation 3 (6.9g) in dry sulpholane (21 cm^3) was treated with dry potassium fluoride (2.0g) and tetraphenylphosphonium bromide (catalyst; 0.18g). The mixture was stirred and heated to 200-205° under an atmosphere of nitrogen for 5 hours. The mixture was cooled to ambient temperature and diluted with water (1 litre) and extracted with hexane (3 x 300 cm^3). The hexane fractions were washed with water (2 x 200 cm^3), dried (anhydrous magnesium sulphate) and the solvent evaporated under reduced pressure to give a mixture containing the above products in the ratio 8:1 (A:B) as a brown liquid, together with unreacted 3,5-dichlorobenzenesulphurpentafluoride present in the starting material. The proportion of the product (B) obtained in repeat preparations was variable. Unless indicated otherwise, the minor product (B) was usually eliminated during subsequent reaction and isolation or purfication of end-products obtained using the product of Preparation 4 as a starting material.

A) Molecular ion 290
(B) Molecular ion 274
^{1}H NMR δ($CDCl_3$) (A) 7.77(d)

PREPARATION 5

Preparation of 4-amino-3-bromobenzenesulphurpentafluoride

4-Aminobenzenesulphurpentafluoride (11.0g) in acetonitrile (dry; 140 cm^3) was stirred at ambient temperature and treated with a solution of N-bromosuccinimide (9.0g) in acetonitrile (90 cm^3) over 7 hours. The mixture was stored at ambient temperature for 18 hours, and the solvent evaporated under reduced pressure. The residue was partitioned between diethyl ether (300 cm^3) and aqueous sodium bicarbonate (200 cm^3). The ether fraction was washed with water, dried (anhydrous magnesium sulphate) and evaporated under reduced pressure to give the required product as a fawn solid.

melting point (hexane) 62.5-63.5°.
^{1}H NMR δ($CDCl_3$) 4.4(b,2H), 6.74(d,1H), 7.50(dd,1H), 7.82(d,1H).

Molecular ion 297.

PREPARATION 6

Preparation of 4-Amino-3-cyanobenzenesulphurpentafluoride

4-Amino-3-bromobenzenesulphurpentafluoride (12.4g) in dry N-methylpyrrolidin-2-one (dry; 20 cm^3)) was treated with copper (I) cyanide (4.0g) under an atmosphere of nitrogen. The mixture was stirred at 160-170° for 17 hours, cooled to ambient temperature and diluted with aqueous ammonia. The mixture was extracted with diethyl ether (3 x 250 cm^3) and the combined extracts washed with water (2 x 300 cm^3) and dried (anhydrous magnesium sulphate). The solvent was evaporated under reduced pressure to give the required product as a brown solid.

A portion was further purified by chromatography (silica gel; hexane/ethyl acetate 7:3 by volume).

Melting point 122-4°.

^1H NMR $\delta(CDCl_3)$ 4.7(broad signal 2H), 6.76(d,1H), 7.68(dd,1H), 7.80(d,1H).

Molecular ion 244.

PREPARATION 7

Preparation of 4-Amino-3-chloro-5-cyano-benzenesulphurpentafluoride

4-Amino-3-cyanobenzenesulphurpentafluoride (7.0g) in carbon tetrachloride (4g) was stirred and treated at ambient temperature with chlorine (4g).

The reaction mixture was stored for 48 hours, the solvent evaporated under reduced pressure, the residue washed with hexane and filtered to give the required product as a yellow solid.

Molecular ion 278.

Melting point 102-3°.

^1H NMR $\delta(CDCl_3)$ 5.2(broad signal,2H), 7.76(d,1H), 7.85(d,1H).

PREPARATION 8

Preparation of 3-Cyano-4,5-dichlorobenzenesulphurpentafluoride

The material from Preparation 7 (5.3g) in acetonitrile (dry, 40 cm^3) was added dropwise over 0.5 hour to a stirred mixture of copper (II) chloride (3.23g) and tertiary butyl nitrite (3.56 cm^3) in acetonitrile (dry; 50 cm^3) at 60-5° under an atmosphere of nitrogen. On complete addition the reaction was heated for a further 0.5 hour at 60°, cooled, poured into water (750 cm^3), acidified with concentrated hydrochloric acid

and extracted with hexane/diethylether (1:1 by volume; 3 x 200 cm^3). The organic fractions were combined, washed with water (3 x 200 cm^3), dried (anhydrous magnesium sulphate) and evaporated under reduced pressure to give an oil. The oil was distilled at 140-5° at 12mm Hg to give an oil which solidified on cooling, (3.97g) and contained 3-chloro-5-cyano--benzenesulphurpentafluoride (A) (6%) and the required product (B) (94%).

Molecular ions (A) 263

(B) 297

^1H NMR $\delta(CDCl_3)$ (B) 8.00(d,1H), 8.10(d,1H).

PREPARATION 9

Preparation of Ethyl N-(2,6-dichlorobenzene 4-pentafluorosulphanyl)--formimidate

4-Amino-3,5-dichlorobenzenesulphurpentafluoride (20g) was treated with triethylorthoformate (38.6 cm^3) and p-toluenesulphonic acid hydrate (catalyst; 0.75g). The mixture was heated to 110° and ethanol removed by distillation during the reaction. The excess orthoformate was evaporated under reduced pressure to give an oil containing the required product. Molecular ion 343.

PREPARATION 10

Preparation of N-cyanomethyl-N'-(2,6-dichlorobenzene-4-pentafluoro-sulphanyl)-formamidine

The material from Preparation 9 (22g) was dissolved in dry tetrahydrofuran (90 cm^3) and treated with aminoacetonitrile (4.3g) in dry tetrahydrofuran (90 cm^3) over 3 hours.

The reaction was stirred and heated to reflux under an atmosphere of nitrogen for 18 hours, further aminoacetonitrile (3.4g) in tetrahydrofuran (50 cm^3) added over 4 hours and heated for a further 1 hour on complete addition. The solvent was evaporated under reduced pressure, the residue taken into water and extracted with dichloromethane (400 cm^3). The organic fraction was washed with water, dried (magnesium sulphate) and evaporated under reduced pressure to give a solid. The solid was washed with hexane, filtered, washed with further hexane and dried to give the required product as a purple solid.

^1H NMR $\delta(CDCl_3)$ 4.40(2H,broad signal), 4.85-5.45(1H,broad signal), 7.62(1H,s), 7.72(2H,s).

PREPARATION 11

5-amino-3-cyano-4-trifluoromethylthio-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)pyrazole

Stage 1

4-amino-3,5-dichlorophenylsulphurpentafluoride (1.00g - Preparation 2) in acetic acid (2.5cm^3) was added at 25-30°C over 30 minutes to a previously prepared solution of sodium nitrite (0.265g) in concentrated sulphuric acid (1.4cm^3) and glacial acetic acid (1.25cm^3), held at 35-40°C and then cooled to ambient temperature.

On complete addition the stirred mixture was heated to 55°C for 30 minutes, cooled to ambient temperature, and added to a mixture of ethyl 1,2-dicyano propionate (0.64g), acetic acid (3cm^3) and water (6.25cm^3) at 10-20°C. The reaction mixture was stirred at ambient temperature for 20 minutes, poured into water (15cm^3) and extracted with dichloromethane (3 x 7cm^3). The combined extracts were washed with aqueous (0.88) ammonia (1.5cm^3) and the organic phase treated with further ammonia solution (1 cm^3) and stirred for 18 hours at ambient temperature. The organic phase was separated, washed with water (twice), dried over anhydrous magnesium sulphate and evaporated under reduced pressure to give a brown gum. The gum was fractionated by eluting through a short column of silica gel with dichloromethane/hexane (3:1 by volume) to give the desired product as a pale yellow solid. ^1H NMR $\delta(CDCl_3)$ 7.93(s,2H), 6.05(s,1H), 3.7-3.8(broad singlet,NH_2). Molecular ion 378.

Stage 2

The product of stage 1 (0.29g) in dry dichloromethane (8cm^3) was stirred and cooled to -14°C. Trifluoromethylsulphenyl chloride was slowly bubbled into the solution and retained at reflux using a carbon dioxide/acetone cold trap. The solution was allowed to reach ambient temperature and was stirred for 1½ hours, poured into water (50cm^3) and treated with aqueous sodium hydrogen carbonate. The mixture was extracted with diethyl ether (three times) and the combined extracts washed with water, dried over anhydrous magnesium sulphate and evaporated under reduced pressure to give a pale yellow solid. The solid was fractionated by eluting through a short column of silica gel with dichloromethane/hexane (1:1 by volume) to give the desired product as a colourless solid. Melting point 184.9-186.8°: NMR $CDCl_3$ δ7.95(2H,s); 4.35-4.50(broad singlet,2H).

Molecular ion 478.

PREPARATION 12

Preparation of 1-(2,6-dichloro-4-pentafluorosulphanylphenylamino)-2,3--dicyano-prop-1-ene

4-amino-3,5-dichlorophenylsulphurpentafluoride (17.3g) was melted and added to a stirred solution of para-toluenesulphonic acid monohydrate (13.7g) and acetic anhydride (7.4g) in glacial acetic acid (10cm^3) at 20°C, under a nitrogen atmosphere. A solution of crude 1-(dimethylamino)-2,3-dicyanoprop-1-ene (13.9g - prepared as described in EP 0460940) in glacial acetic acid (30cm^3) was added dropwise at 25 to 27°C. The mixture was stirred at room temperature for 20 hours, then poured into stirred water (200cm^3). The mixture was extracted with ether (4 x 200cm^3), the combined extracts washed with saturated brine (50cm^3), dried over magnesium sulphate, filtered and concentrated under reduced pressure to give a solution of the crude product in acetic acid. Crystals formed on standing which were filtered off, washed with acetic acid (3 x 20cm^3), hexane (3 x 20cm^3) and air-dried to give the desired product as a white solid (6.3g). Melting point 121 to 123°C. Molecular ion 377.

EXAMPLE 1

Stage 1: Preparation of 5-Amino-1-(2,6-dichlorobenzene-4-pentafluoro-sulphanyl)imidazole

The material from Preparation 10 (5.5g) was dissolved in dry methanol (350 cm^3) under an atmosphere of nitrogen and treated over 0.5 hour with sodium methoxide (1.08g) in methanol (50 cm^3) at 0°, stirred at 0° for 2 hours and at ambient temperature for 1 hour. The solvent was evaporated under reduced pressure and the residue treated with water (100 cm^3) and extracted with dichloromethane (2 x 300 cm^3). The organic fractions were dried (magnesium sulphate) and evaporated under reduced pressure to yield the required product as an oil, which partially solidified on storing.
^{1}H NMR δ($CDCl_3$) 3.0(2H,broad signal), 6.70(1H,s), 7.22(1H,s), 7.92(2H,s).

Stage 2: Preparation of 5-Amino-1(2,6-dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoro-methylsulphenylimidazole (Compound No 6 of Table I)

The material from Stage 1 (5.5g) was dissolved in dry 1,2-dichloroethane (350 cm^3) and treated at -20° with trifluoromethyl sulphenyl chloride (4.5g). The reaction was allowed to warm to ambient temperature and stored for 18 hours. The solvent was evaporated under reduced pressure and the residue partitioned between ethyl acetate and water. The organic fraction was dried (magnesium sulphate), evaporated under reduced pressure and fractionated using chromatography (silica gel; hexane/ethyl acetate; 9:1 and 4:1 by volume) to give the required product as a solid.

melting point 175.8-177.2°.

^1H NMR $\delta(CDCl_3)$ 3.7(2H, broad signal), 7.20(1H,s), 7.95(2H,s).

Molecular ion 433.

EXAMPLE 2

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoro--methylsulphenylmidazole (Compound No 7 of Table 1)

The product from Example 1 (2.5g) in tetrahydrofuran (dry; 50 cm^3) containing tertiary butylnitrite (3.3cm^3) was stirred under an atmosphere of nitrogen and heated to reflux for 2 hours. The reaction was cooled, evaporated under reduced pressure, and the residue dissolved in ethyl acetate and washed with water. The organic fraction was dried (magnesium sulphate) and re-evaporated to give a brown oil. A portion (1.5g) was fractionated using chromatography (silica gel hexane/ethyl acetate, 4:1 by volume) to give the required product as a pale yellow solid.

Melting point 93.6-95.5°.

^1H NMR $\delta(CDCl_3)$ 7.40(1H,broad singlet), 7.65(1H,broad singlet), 7.93(2H,s). Molecular ion 438.

The remaining material (1.5g) was used without further purification in Example 3.

EXAMPLE 3

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoro-methylsulphinyl-imidazole (Compound No 8 of Table 1)

The material from Example 2 (1.5g) was dissolved in dichloromethane (dry; 20 cm^3) and cooled to 0°. Meta chloroperbenzoic acid (1.05g; 80% strength) was added in portions to the above stirred solution, and held for an additional 1 hour at 0°. The reaction was allowed to warm to ambient temperature and was stirred for 60 hours. The mixture was diluted with

ethyl acetate (200 cm^3), washed with aqueous sodium hydrogen carbonate, and water (twice) and dried (magnesium sulphate). The solvent was evaporated under reduced pressure and the residual gum fractionated using chromatography, (silica gel hexane/ethyl acetate 4:1 by volume), to give the required product;

Melting point 127.1-128.5°.

^1H NMR $\delta(CDCl_3)$ 7.72(1H,s), 7.75(1H,s), 7.95(2H,s).

Molecular ion 454.

Another fraction (0.28g) containing recovered starting material and 1(2,6-dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoromethy-sulphonylimidazole was treated as described in Example 25.

EXAMPLE 4

Preparation of 1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-2-methyl-4--trifluoromethylimidazole (Compound No 3 of Table 1)

To a stirred supension of sodium hydride (0.12g; 50% oil dispersion in dry N-methylpyrrolidin-2-one (10 cm^3) at 0° under an atmosphere of nitrogen was added 2-methyl-4-trifluoromethyliimidazole (0.37g).

The mixture was stirred at 20° for 0.17 hour and treated dropwise with 3,4,5-trichlorobenzene-sulphurpentafluoride (0.85g; 90% pure - Preparation 3) in dry N-methylpyrrolidin-2-one (10 cm^3). The reaction mixture was heated to 60° for 36 hours, cooled, diluted with water and extracted with diethyl ether (3 times). The combined diethylether fractions were washed with water (3 times) dried (anhydrous magnesium sulphate) and the solvent evaporated under reduced pressure. The residual brown oil was fractionated using chromatography (silica gel; hexane/ethyl acetate 7:3 by volume) to give the required product as a pale yellow solid.

Melting point 126.2-127.2°.

^1H NMR $\delta(CDCl_3)$ 2.25(3H,s), 7.20(1H,s), 7.93(2H,s).

EXAMPLE 5

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-2-methyl-4--pentafluoroethylimidazole (Compound No 4 of Table 1)

2-Methyl-4-pentafluoroethylimidazole was reacted with 3,5-dichloro-4-fluorobenzenesulphurpentafluoride (Preparation 4) using the general method of Example 4. The 2-Methyl-4-pentafluoroethylimidazole starting material was prepared by reaction of 2-methylimidazole with pentafluoroethyl iodide

using the method described in J. Org.Chem. (1982)47 2867.

Melting point 165.5-166.9°

^{1}H NMR δ($CDCl_3$) 2.25(3H,s), 7.20(1H, 7.93(2H,s). Molecular ion 470.

EXAMPLE 6

Preparation of 1(2-Chloro-6-cyanobenzene-4-pentafluorosulphanyl)-4--trifluoromethyl-imidazole (Compound No 5 of Table 1)

1(H)-4-Trifluoromethylimidazole was reacted with 3-cyano-4,5-dichlorobenzenesulphurpentafluoride (Preparation 8) using the general method of Example 4.

Melting point 154.1-155.4°

^{1}H NMR δ($CDCl_3$) 7.50(1H,s), 7.75(1H,s), 8.15(1H,d), 8.25(1H,d).

EXAMPLE 7

Preparation of 3-Cyano-1(2.6-dichlorobenzene-4-pentafluorosulphanyl)-5--thiomethyl-4-trifluoromethylsulphenylpyrazole (Compound No 14 of Table II)

5-Amino-3-cyano-4-trifluoromethylthio-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)pyrazole (0.285g - Preparation 11) in dichloromethane (dry 5 cm^3) was treated with dimethyldisulphide (0.28g) and cooled to 0°. Tertiary butylnitrite (0.068g) in dichloromethane (1cm^3) was added dropwise to the stirred solution under an atmosphere of nitrogen. On complete addition the reaction was stored at 5° for 18 hours and the solvent was evaporated under reduced pressure. The residue was fractionated using chromatography (silica gel; hexane/ethyl acetate 9:1 by volume) to give the required product as a yellow solid.

Melting point 108.6-109.8.

^{1}H NMR δ($CDCl_3$) 2.43(3H,s), 7.95(2H,s). , Molecular ion 509.

EXAMPLE 8

Preparation of 1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-cyano-4--trifluoromethylsulphinyl-5-[(4-hydroxy-3-methoxyphenyl)-methylidene-imino]pyrazole (Compound No 17 of Table II)

5-Amino-3-cyano-4-trifluoromethylthio-1-((2,6-dichlorobenzene-4-pentafluorosulphanyl)pyrazole (0.20g) in toluene (50cm^3) containing 4-hydroxy-3-methoxybenzaldehyde (0.083g) and para toluene sulphonic acid hydrate (0.01g; catalyst) were stirred and heated to reflux for 36 hours. Water produced during the reacion was collected in a Dean and Stark trap. The solvent was evaporated under reduced pressure and the residue extracted into ethylacetate, washed with aqueous sodium carbonate, water and dried

(anhydrous magnesium sulphate). The required product was obtained as a pale yellow solid.
^{1}H NMR δ($CDCl_3$): 3.90(3H,s), 6.15(1H,s), 6.95-7.05(1H,dd), 7.2[1H under $CHCl_3$ signal], 7.30-7.35(1H,dd), 7.90(2H,s), 8.93(1H,s).
Molecular ion 612.

EXAMPLE 9

Preparation of 2-Amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluoro-sulphanyl)pyrrole (Compound No 18 of Table III)

A solution of 1-(2,6-dichlorobenzene-4-pentafluorosulphanylamino)-2,3-dicyanoprop-1-ene [5.66g - Preparation 12] and triethylamine [1.51g] in toluene [60cm^3] was stirred at 80°C for 6 hours under a nitrogen atmosphere. Toluene and triethylamine were evaporated under reduced pressure to leave a solid which was recrystalised from ether/hexane solution to give the desired product as a buff solid.
Melting point 150 to 151°C. ^{1}H NMR δ($CDCl_3$): 7.9(2H,s), 6.8(1H,d), 5.9(1H,d), 3.1(2H,br.s). Molecular ion 377.

EXAMPLE 10

Preparation of 2-amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluoro-sulphanyl)pyrrole (compound No 19 of Table III)

A sollution of dichlorofluoromethylsulphenylchloride [4.6g] in dichloromethane [20cm^3] was added dropwise to a stirred solution of the product of Example 9 [10.0g] in dichloromethane [80cm^3], at 15°C, under a nitrogen atmosphere. After 20 hours at 20°C the solution was washed with saturated aqueous sodium hydrogen carbonate [50cm^3], dried over magnesium sulphate, filtered and the solvent evaporated under reduced pressure to leave a solid which was recrystallised from dichloromethane/hexane to give the desired product as a light brown solid. Melting point 188 to 190°C.
^{1}H NMR δ($CDCl_3$): 7.95(2H,s), 6.85(1H,s), 4.0(2H,br.s). Molecular ion 509.

EXAMPLE 11

Preparation of
2-amino-5-chloro-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)--3-dichlorofluoromethylthiopyrrole (compound No 20 of Table II)

A solution of sulphuryl chloride [3.4g] in dichloromethane [20cm^3] was added dropwise to a stirred solution of the product of Example 10 [12.9g] in dichloromethane [180cm^3], at 22°C under a nitrogen atmosphere. The mixture was allowed to stand for 20 hours. The solution was washed with

saturated aqueous sodium hydrogen carbonate [50cm^3] dried over magnesium sulphate, filtered and evaporated under reduced pressure to leave a solid which was recrystallised from dichloromethane/hexane to give the desired product as a light brown solid. Melting point 203°C.
^{1}H NMR δ($CDCl_3$): 8.0(2H,s), 4.0(2H,br.s). Molelcular ion 543.

EXAMPLE 12

Preparation of 2-amino-5-chloro-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-dichlorofluorosulphinylpyrrole (Compound No 21 of Table III)

A solution of meta-chloroperoxybenzoic acid [3.3g] in dichloromethane [50cm^3] was added dropwise to a stirred solution of the product of Example 11 [10.0g] in dichloromethane [200cm^3], at 4°C. The mixture was allowed to stand at 5°C for 24 hours. The solution was stirred with saturated aqueous sodium hydrogen carbonate [32cm^3] and 1M sodium sulphite [16cm^3] whereupon an emulsion formed. Sufficient magnesium sulphate to absorb all the water was added, the mixture filtered, the residue washed with dichloromethane and the filtrate plus washings evaporated under reduced pressure to leave the crude product. The product was purified using column chromatography on silica gel, eluting with dichloromethane to give a light brown solid [2.0g].
Melting point 207°C (with decomposition). ^{1}H NMR δ($CDCl_3$): 8.0(2H,s), 4.95(2H,br.s). Molecular ion 559.

EXAMPLE 13

Preparation of 5-chlor-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-dichlorofluoromethylsulphinyl-2-methylthiopyrrole (Compound No 22 of Table III)

To a stirred solution of the product of Example 12 [1.68g] and dimethyldisulphide [1.4g] in chloroform [50cm^3], at 5°C, was added dropwise, tert-butylnitrite [0.34g]. The mixture was allowed to stand at 5°C for 20 hours. Volatile materials were evaporated under reduced pressure to leave the crude product. The product was purified using column chromatography on silica gel eluting with ether/hexane mixtures followed by recrystallisation from dichloromethane/hexane to give a yellow solid.
Melting point 204°C. ^{1}H NMR: δ($CDCl_3$): 8.0(2H,d), 2.25(3H,s). Molecular ion 590.

EXAMPLE 14

Preparation of 2-amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3,5-bis(trifluoromethylthio)pyrrole (Compound No 23 of Table III) and 2-amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)--3-trifluoromethylthiopyrrole (Compound No 24 of Table III)

Trifluoromethylsulphenyl chloride [about 8g] was bubbled into a stirred solution of 2-amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphinyl)pyrrole [2.06g - Example 9] in dichloromethane [40cm^3] for 10 minutes at 5°C. After stirring for another 45 minutes at 5°C, saturated aqueous sodium hydrogen carbonate [100cm^3] was added and the mixture was thoroughly stirred. The layers were separated, the aqueous extracted with dichloromethane [3 x 80cm$_3$], the combined dichloromethane solutions dried over magnesium sulphate, filtered and solvent evaporated under reduced pressure to leave a pale brown solid. The solid was subject to column chromatography on silica gel, eluting with dichloromethane/hexane mixtures to obtain the pure products as white solids.

2-Amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3,5-di(triflormethylthio)pyrrole: Melting point 166°C;
^{1}H NMR δ(CDCl$_3$): 8.0(s). Molecular ion 577.

2-amino-4-cyano-1-(2,6-dichloro-4-pentafluorosulphenylphenyl)-3-trifluoromethylthiopyrrole: Melting point 188-9°C;
^{1}H NMR δ(CDCl$_3$): 7.95(2H,s), 6.85(1H,s); Molecular ion 477.

EXAMPLE 15

Preparation of 4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-2-methylthio-3,5-bis(trifluoromethyl)pyrrole (Compound No 28 of Table III)

2-Amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3,5-bis(trifluoro-methylthio)pyrrole [1.0g, Example 14] was treated with dimethyldisulphide using the general method of Example 13 to give the desired product as a yellow solid. Melting point 130-1°C.
^{1}H NMR δ(CDCl$_3$): 7.95(2H,s), 2.3(3H,s). Molecular ion 608.

EXAMPLE 16

Preparation of 2-amino-5-chloro-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-trifluoromethylthiopyrrole (Compound No 27 of Table III)

2-Amino-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-trifluoromethylthiopyrrole [0.11g, Example 14] was treated with thionyl

chloride using the general method of Example 11 to give the desired product as a solid mixed with a small amount of the starting material.
Melting point 183-6°C. ^{1}H NMR δ($CDCl_3$), major component: 8.0(2H,s), 3.9(2H,br.s). Molecular ion (major component) 511.

EXAMPLE 17

Preparation of 5-chloro-4-cyanol-(2,6-dichlorobenzene-4-pentafluoro-sulphanyl)-3-dichlorofluoromethylthiopyrrole (Compound No 26 of Table III)

To a stirred solution of the product of Example 16 [2.03g] in tetrahydrofuran [35cm^3], under a nitrogen atmosphere, was added dropwise at 5°C, a solution of tert-butylnitrite [0.42g] in tetrahydrofuran [5cm^3]. The mixture was allowed to warm to 20°C over 2½ hours then refluxed for 1½ hours. The solvent was evaporated under reduced pressure to leave the crude desired product which was purified by column chromatography on silica gel, eluting with hexane 9:1 ether to give a white solid.
Melting point 147-8°C. ^{1}H NMR δ($CDCl_3$): 7.95(2H,s), 7.05(1H,s).
Molecular ion 528.

EXAMPLE 18

Prepaation of 2-bromo-5-chloro-4-cyano-1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-dichlorofluoromethylthiopyrrole (Compound No 25 of Table III)

To a stirred solution of the product of Example 16 [1.0g] and copper (II) bromide [0.82g] in acetonitrile [20cm^3] at 5°C, under a nitrogen atmosphere was added a solution of tert-butylnitrite [0.21g] in acetonitrile [3cm^3]. The mixture was allowed to warm to 20°C over 2 hours and continued to stir for 20 hours. The product was refluxed for 5 minutes, and acetonitrile evaporated under reduced pressure to leave a solid residue which was subject to column chromatography on silica gel, eluting with hexane : dichloromethane 7:3 to give the desired product as a white solid. Melting point 180-1°C; ^{1}H NMR δ($CDCl_3$) 8.0(s).
Molecular ion 606.

EXAMPLE 19

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoro--methylpyrimidin-6-one (Compound No 29 of Table IV)

Sodium hydride (0.077g; 50 % oil dispersion; washed with hexane) was stirred under an atmosphere of nitrogen in dry N,N-dimethylformamide (5 cm^3) and treated with 1(H)-4-trifluoromethylpyrimidin-6-one at ambient

temperature. The mixture was stirred for 0.5 hour to give a pale yellow solution. 3,5-Dichloro-4-fluorobenzenesulphurpentafluoride (Preparation 4; 0.70g) in dry N,N-dimethylformamide (0.5 cm^3) was added and the reaction heated to 90° for 6 hours, cooled and stored for 18 hours. The reaction was diluted with water, acidified with dilute hydrochloric acid and extracted with ethyl acetate. The organic fractions were combined, washed with water, brine, dried (magnesium sulphate) and evaporated under reduced pressure to give a brown solid. The solid was fractionated using chromatography [silica gel; hexane/ethyl acetate 4:1 by volume] to give a yellow solid which was washed with hexane to give the required product as a colourless solid.

Melting point 156.3-157.3.

^1H NMR $\delta(CDCl_3)$: 7.00(^1H,s), 7.96(2H,s), 8.00(1H,s)

EXAMPLE 20

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4-pentafluoroethylpyrimidin-6-one (Compound No 30 of Table IV).

The title compound was prepared using the general method of Example 19 by reaction of 1(H)-4-pentafluoroethylpyrimidin-6-one (0.343g).

Melting point 202-203°. ^1H NMR $\delta(CDCl_3)$: 7.07(1H,s), 7.98(2H,s), 8.00(1H,s).

^{19}F NMR 62 ppm d (4F), 79 ppm multiplet (1F), -83 ppm s (2F), -120 ppm s (3F).

EXAMPLE 21

Preparation of 1-(2,6-dichlorobenzene-4-pentafluorosulphanyl)-3-chloro-5--trifluoromethylpyrid-2-one (Compound No 31 of Table V).

3-Chloro-5-trifluoromethylpyrid-2-one (0.30g) and the product of Preparation 4 in dry N,N-dimethylformamide (2.5 cm^2) containing anhydrous potassium carbonate (0.65g) was stirred and heated in a Wheaton vial to 110° for 4½ hours. The reaction mixture was cooled, poured into water (100 cm^3), extracted with diethyl ether (2X 100 cm^3) and the combined ether fractions were washed with water (2 x 75 cm^3) and dried (anhydrous magnesium sulphate). The solvent was evaporated under reduced pressure and the residue fractionated using chromatography (silica gel; hexane/ethyl acetate 9:1 by volume) to give the required product as a colourless solid. The product contained a minor proportion of 1-(2-chlorobenzene-6-fluoro-4-pentafluorosulphanyl)-3-chloro-5-

-trifluoromethylpyrid-2-one derived from the minor product of Preparation 4.

Melting point 158.5-159.7°. ^{1}H NMR δ($CDCl_3$): 7.40(1H,d), 7.80(1H,d), 7.93(2H,s). Molecular ion 467.

EXAMPLE 22

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-imidazole (Compound No 1 of Table I)

Imidazole (0.55g) was added at ambient temperature to a stirred suspension of sodium hydride (0.39g; 50% oil dispersion) in N-methyl-pyrrolidin-2-one (dry,; 20cm^3) under an atmosphere of nitrogen. The mixture was stirred for 10 minutes and a solution of 3,4,5-trichlorobenzenesulphurpentafluoride (2.50g) in N-methylpyrrolid-2-one (10cm^3) was added slowly dropwise. On complete addition the reaction was heated to 60-5°C for 2.75 hours, cooled, diluted with water and extracted with ethyl acetate. The organic factions were combined, washed with water, dried and evaporated under reduced pressure. The residual liquid was re-dissolved in diethyl ether (300cm^3), washed with water, dried and evaporated under reduced pressure to give a brown solid which was fractioned using chromatography (silica gel hexane/ethyl acetate 7:3 by volume) to give the required product.

Melting point 137.8-139.5°C. Molecular ion 338.

^{1}H NMR δ($CDCl_3$) 7.05(1H,s); 7.30(1H,s); 7.75(1H,s); 7.90(2H,s).

EXAMPLE 23

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)--4-trifluoromethylimidazole (Compound No 2 of Table 1)

The title compound was prepared using the general method of Example 4.

Melting Point 165-166°C. Molecular ion 406. ^{1}H NMR ($CDCl_3$): 7.38 (1H,s); 7.60(1H,s); 7.93(2H,s).

EXAMPLE 24

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-2-dichlorofluoromethylsulphenylimidazole.

The material from Example 22 (1.26g) in dichloromethane (10cm^3, dry) was treated dropwise at ambient temperature with dichlorofluoromethylsulphenyl chloride (0.67g) in dichloromethane (dry; 4cm^3) with stirring. The mixture was stirred for 60 hours, and further dichlorofluoromethylsulphenyl chloride (0.224g) in dichloromethane (1cm^3)

added at 24 hour and 48 hour intervals. The mixture was diluted with dichloromethane, washed with diluted hydrochloric acid, water and dried (magnesium sulphate). The solvent was removed under reduced pressure, the residual solid dissolved in diethyl ether, washed with water, dried, evaporated and the residual solid fractionated using chromatography (silica gel hexane/ethyl acetate 4:1 by volume) to give the required product, 0.295g. Molecular ion 470. ^{1}H NMR δ($CDCl_3$) 7.25 (1H,s); 7.55(1H,s); 7.90(2H,s).

EXAMPLE 25

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4--trifluoromethylsulphonyl imidazole. (Compound No 9 of Table 1)

The fraction containing recovered starting material and 1(2,6-dichlorobenzene-4-pentafluorosulphanyl)-4-trifluoromethy-sulphonylimidazole (0.28g) obtained as described in Example 3 was dissolved in trifluoroacetic acid (7cm^3) and was treated at 0°C with hydrogen peroxide (30% w/v; 0.12cm^3) with stirring. On addition the mixture was stirred for 1 hour, stored for 18 hours and further hydrogen peroxide (0.05cm^3) added at ambient temperature. The reaction was stirred for 6 hours, stored for 18 hours and concentrated under reduced pressure. The residual liquid was taken into dichloromethane (300cm^3), washed with aqueous sodium metabisulphite, aqueous sodium hydrogen carbonate, water, and dried (magnesium sulphate). The solvent was evaporated under reduced pressure and the solid obtained fractionated using chromatography (silica gel; hexane/ethyl acetate; 4:1 by volume) to give the required product. Melting Point 212.4-213.4°C. Molecular ion 470.
^{1}H NMR δ($CDCl_3$) 7.78(1H,s); 7.97(1H,s); 7.99(2H,s).

EXAMPLE 26

Preparation of 1(2,6-Dichlorobenzene-4-pentafluorosulphanyl)-4-penta-fluoroethyl imidazole (Compound No 11 of Table I)

The title compound was prepared using the general method of Example 5. Melting point 137-138°C. Molecular ion 456.
^{1}H NMR δ($CDCl_3$) 7.50 (1H,s); 7.65(1H,s); 7.95(2H,s).

EXAMPLE 27

Preparation of 1(2-Chloro-6-cyanobenzene-4-pentafluorosulphanyl)-4--pentafluoroethyl imidazole (Compound No 32 of Table I)

The title compound was prepared using the general method of Example 6. Melting point 155.0-156.6°C. Molecular ion 447.

^{1}H NMR δ($CDCl_3$) 7.55(1H,s); 7.85(1H,s); 8.15(1H,d); 8.25(1H,d).

Example 28

Preparation of 1(2-Chloro-6-cyanobenzene-4-pentafluorosulphanyl)-2-methyl-4-pentafluoroethyl imidazole (Compound No 33 of Table I)

The title compound was prepared using the general method of Example 6. Melting point 168.4-169.0°C. Molecular ion 461.

^{1}H NMR δ($CDCl_3$) 8.25(1H,d); 8.15 (1H,d); 2.325 (3H,s)

EXAMPLE 29

The activity of the compounds of the invention was determined using a variety of pests. The pests were treated with a liquid composition containing 500 parts per million (ppm) by weight of the compound. The compositions were made by dissolving the compound in acetone and ethanol (50:50) mixture and diluting the solutions with water containing 0.1% by weight of a wetting agent sold under the trade name "SYNPERONIC" NP8 until the liquid composition contained the required concentration of the compound. "SYNPERONIC" is a Registered Trade Mark.

The test procedure adopted with regard to each pest was basically the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with the compositions. The mortality of the pests was then assessed at periods usually varying from two to five days after the treatment.

The results of the tests are presented in Table VI for each of the compounds. The results indicate a grading of mortality, designated as A, B or C wherein A indicates 80-100% mortality, B indicates 40-79% mortality and C indicates 0-39% mortality. A dash (-) indicates that no data is available. The pest species is designated by a letter code.

Information regarding the pest species, the support medium or food, and the type and duration of the test is given in Table VII.

TABLE VI

Compound No	Tu	Mp	Md	Hv	La	Db
1	C	B	B	C	C	C
2	C	A	-	C	A	C
3	C	A	-	A	A	B
4	B	A	-	A	A	A
9	A	A	-	C	C	B
14	A	A	A	A	A	A
17	A	A	-	A	A	A
18	-	C	B	C	C	-
19	C	A	A	C	C	A
20	B	A	A	A	A	A
21	A	C	A	A	B	-
22	A	B	A	A	A	-
23	C	C	-	C	A	C
24	C	A	-	A	A	A
25	B	A	A	A	A	A
26	A	A	A	A	A	A

TABLE VII

CODE LETTERS	TEST SPECIES	SUPPORT MEDIUM/FOOD	TYPE OF TEST	DURATION (DAYS)
Tu	Tetranychus urticae (spider mite)	French bean leaf	Contact	3
Mp	Myzus persicae (aphid)	Chinese Cabbage leaf	Contact	3
Md	Musca domestica (housefly - adult)	Cotton wool/ sugar	Contact	2

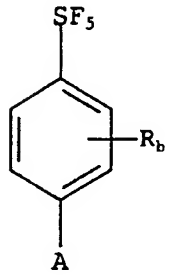
TABLE VII (continued)

CODE LETTERS	TEST SPECIES	SUPPORT MEDIUM/FOOD	TYPE OF TEST	DURATION (DAYS)
Hv	Heliothis virescens (tobacco budworm)	Soya leaf	Residual	5
La	Spodoptera exigua (lesser Army worm)	Cotton leaf	Residual	5
Db	Diabrotica balteata (cucumber beetle - larva)	Filter paper/ maize seed	Residual	2

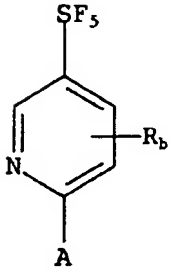
"Contact" test indicates that both pests and medium were treated, "Residual" indicates that the medium was treated before infestation with the pests and "in vitro" indicates that the pest was suspended in an aqueous medium containing the treatment.

CHEMICAL FORMULAE

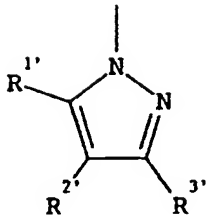
(IN DESCRIPTION)



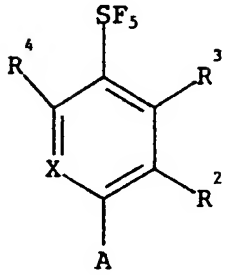
(IA)



(IB)



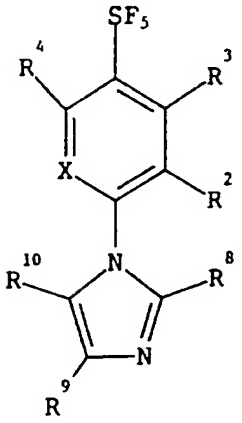
(IC)



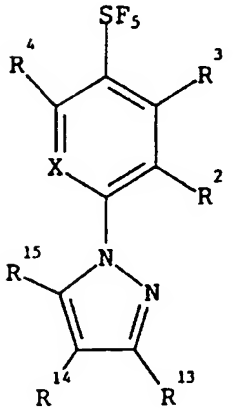
(II)

CHEMICAL FORMULAE

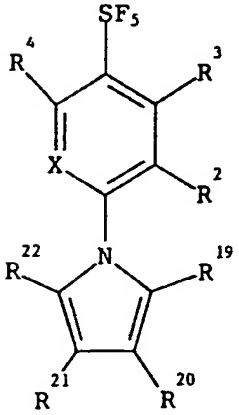
(IN DESCRIPTION)



(III)



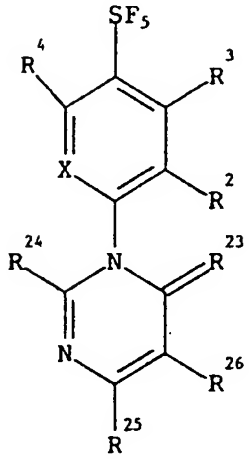
(IV)



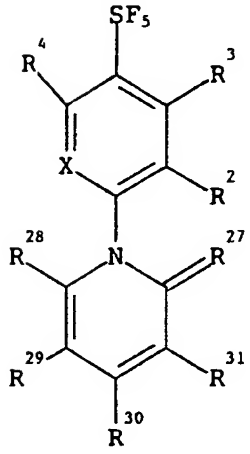
(V)

CHEMICAL FORMULAE

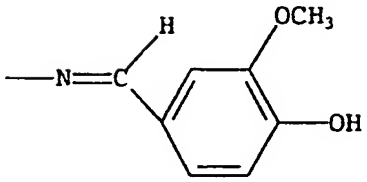
(IN DESCRIPTION)



(VI)



(VII)

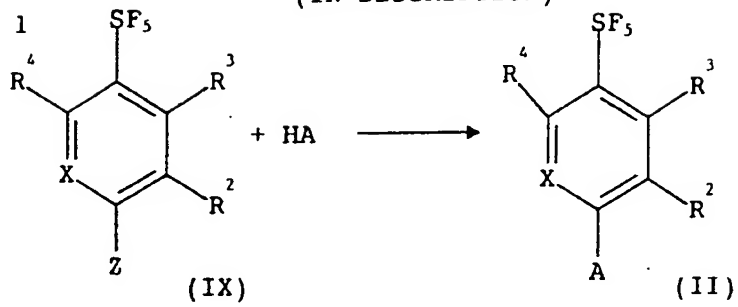


(VIII)

CHEMICAL FORMULAE

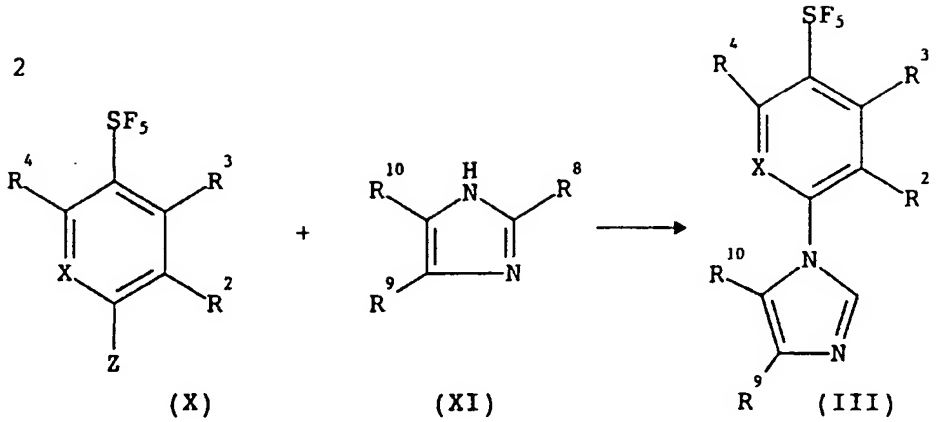
(IN DESCRIPTION)

Scheme 1



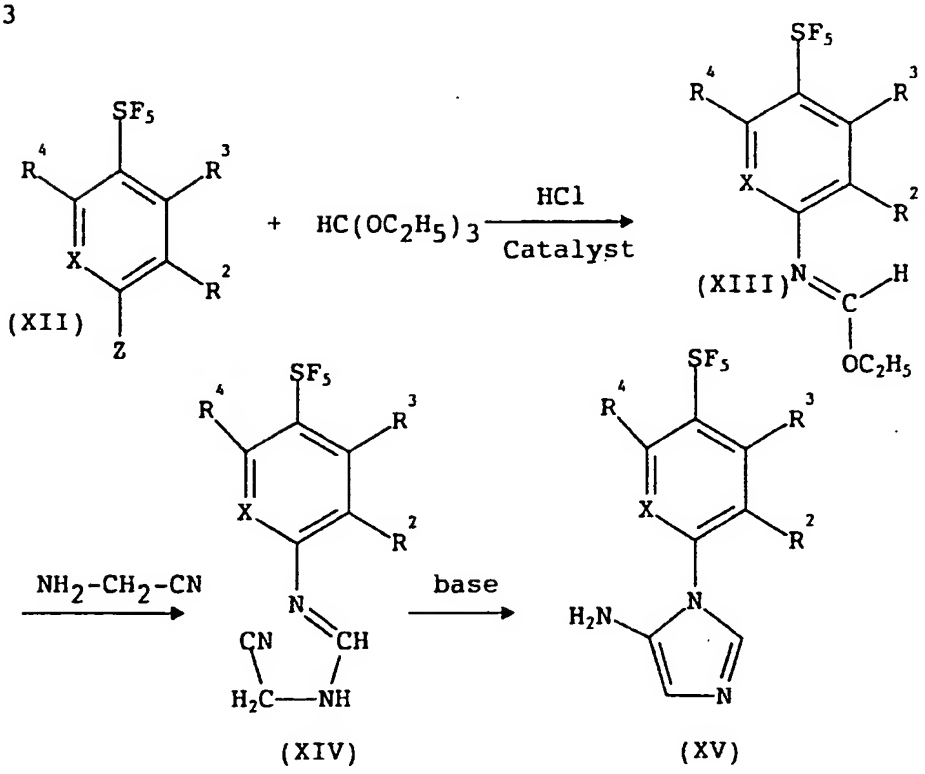
(IX) (II)

Scheme 2



(X) (XI) (III)

Scheme 3

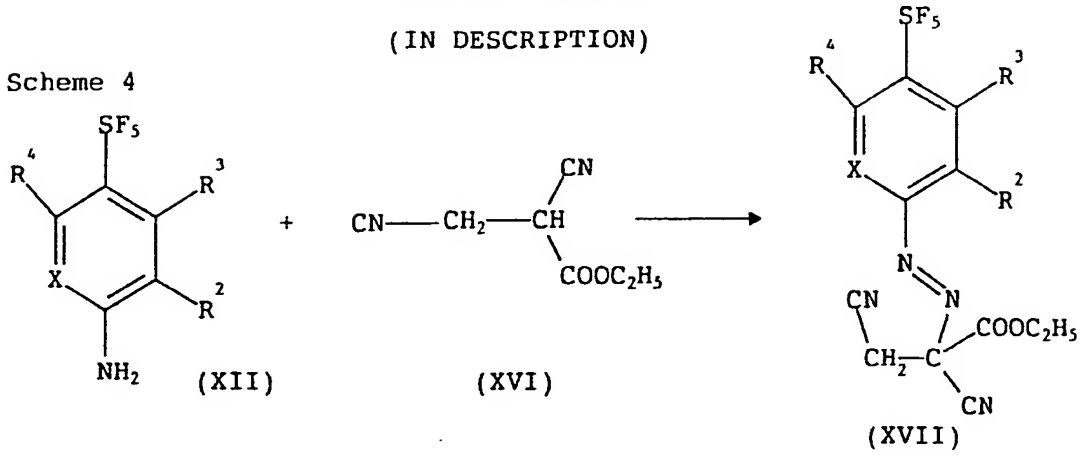


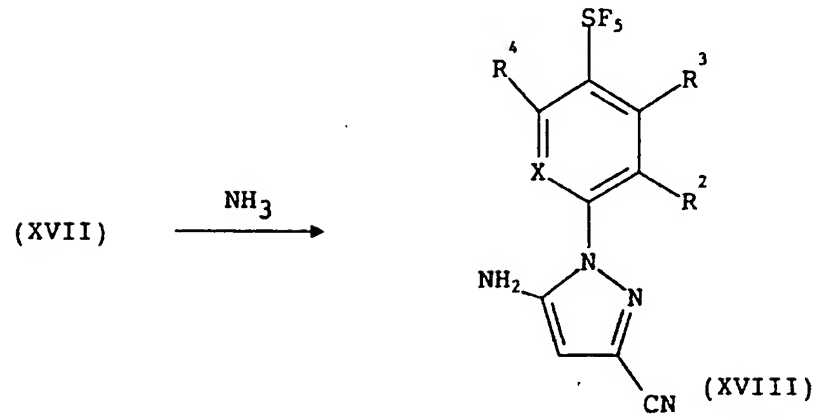
(XIV) (XV)

CHEMICAL FORMULAE

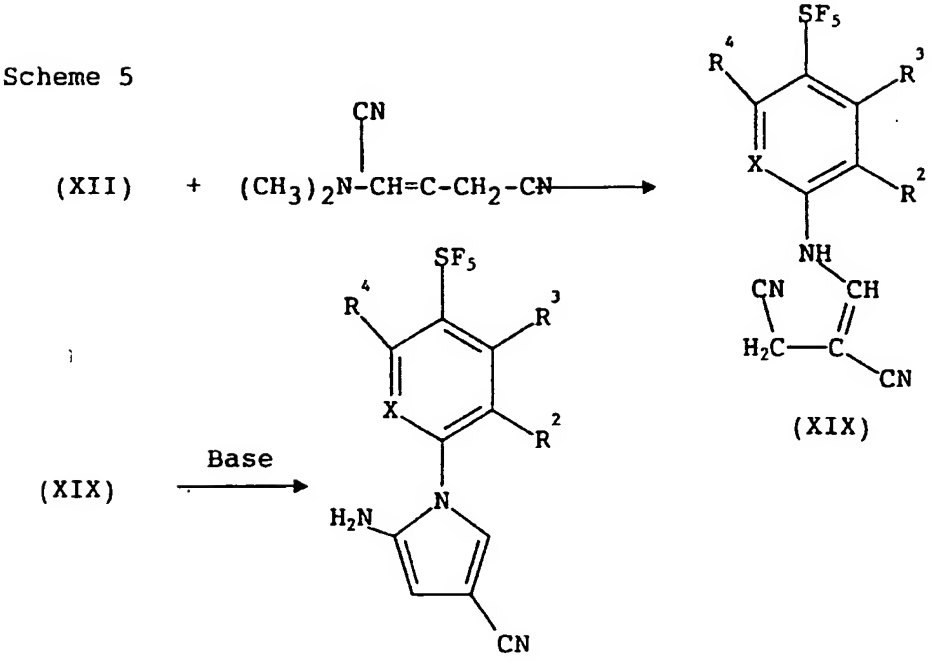
(IN DESCRIPTION)

Scheme 4





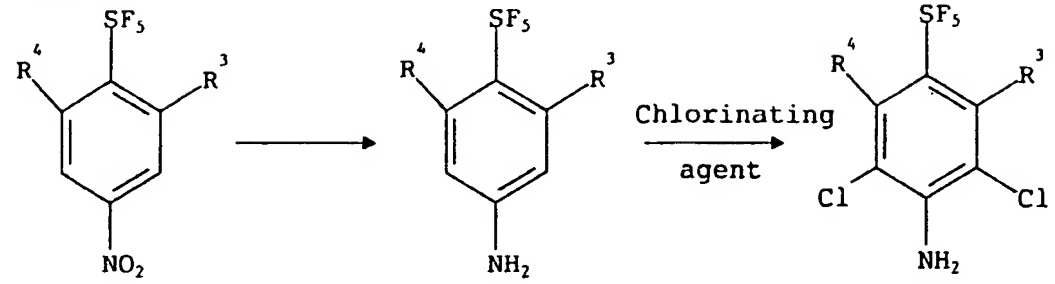
Scheme 5



CHEMICAL FORMULAE

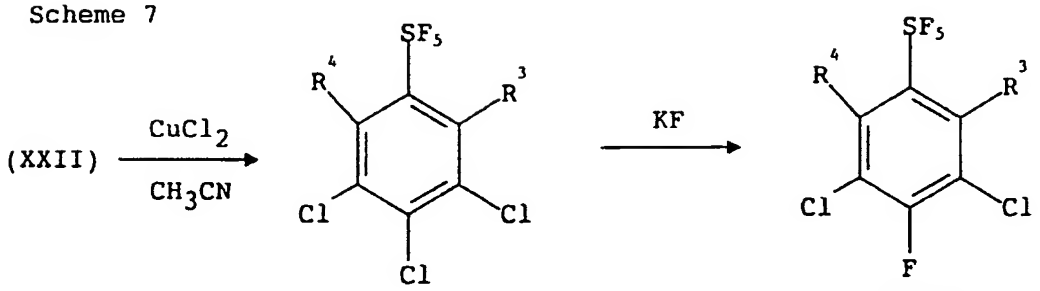
(IN DESCRIPTION)

Scheme 6



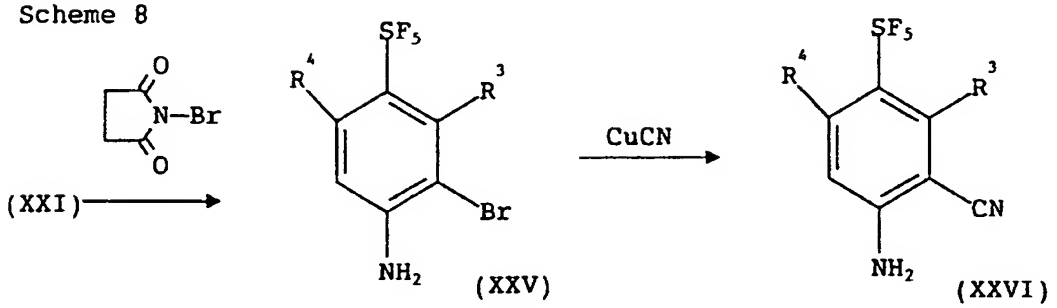
(XXII) (XXI) (XXII)

Scheme 7

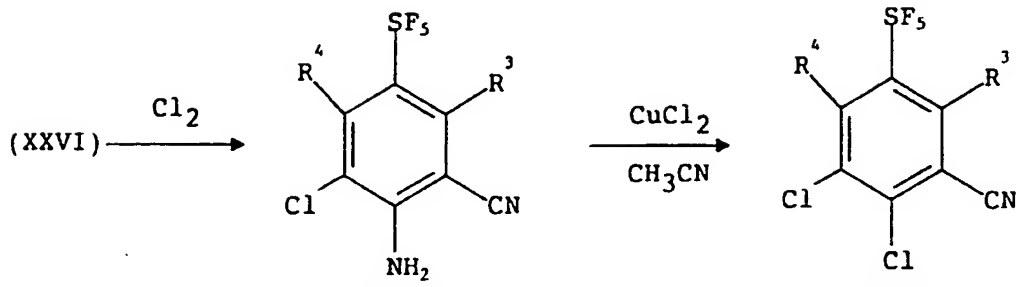


(XXIII) (XXIV)

Scheme 8



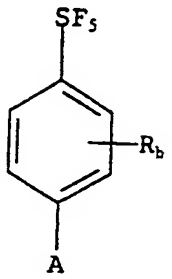
(XXV) (XXVI)



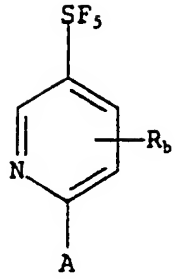
(XXVII) (XXVIII)

CLAIMS

1. A compound of formula (IA) or (IB)

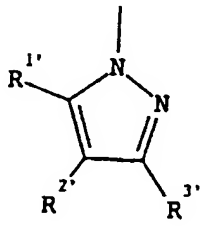


(IA)



(IB)

wherein R_a represents hydrogen or from 1 to 4 optional substituents and R_b represents from 1 to 3 optional substituents and wherein A represents an optionally substituted N-linked nitrogen-containing five or six membered aromatic heterocyclic ring, provided that when the compound is of formula (IA)



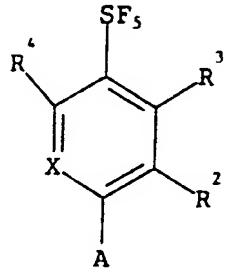
(IC)

and A represents a group of formula (IC) wherein $R^{1'}$ is hydrogen, halogen, or a group $NR^{4'}R^{5'}$ wherein $R^{4'}$ and $R^{5'}$ are independently selected from hydrogen or alkyl; $R^{2'}$ is a group $-S(O)_n{}'R^{6'}$ wherein n' is 0, 1 or 2 and $R^{6'}$ is a haloalkyl group; and $R^{3'}$ is -CN or is a group $CX'-NY^{1'}Y^{2'}$ wherein X' is O or S or S=O; and $Y^{1'}$ and $Y^{2'}$ are independently selected from hydrogen, nitro, amino or alkyl optionally substituted by halogen, by cycloalkyl, by formyl, by C_{2-7} alkanoyl, by C_{4-7} cycloalkylcarbonyl, by C_{2-7} alkoxycarbonyl, by C_{2-7} haloalkoxycarbonyl, by an aryl group or by an aromatic heterocyclic group or

$Y^{1'}$ and $Y^{2'}$ together with the nitrogen to which they are attached form

an aliphatic heterocyclic group containing from 4 to 8 atoms in the ring and optionally substituted by halogen or alkyl or
$Y^{1'}$ and $Y^{2'}$ together form the group $=CHY^3$ wherein Y^3 is alkyl, C_{2-6} alkenyl, aryl, an aromatic heterocycle, or amino optionally substituted by alkyl or
$Y^{1'}$ is hydrogen and $Y^{2'}$ is alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl or a group $-S(O)_{n'}R^{6'}$ where $R^{6'}$ and n' are as hereinbefore defined, then R_a does not represent 2,6-dihalo

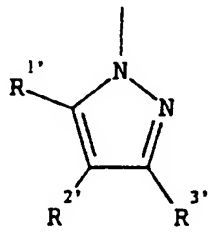
2. A compound of (II)



(II)

wherein X is $-CR^1=$ or $-N=$, R^1 and R^2 are independently selected from hydrogen, halogen, cyano, nitro, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkoxy, optionally substituted alkenyl or optionally substituted alkynyl or from a group $-S(O)_mR^5$ wherein m is 0, 1 or 2 and R^5 is optionally substituted alkyl or from a group $C(Y)-NR^6R^7$ where Y is =O or =S and R^6 and R^7 are independently selected from hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or amino or R^6 and R^7 together with the nitrogen to which they are attached form an optionally substituted aliphatic heterocyclic ring containing from 4 to 8 atoms in the ring, or R^6 and R^7 together form the group $=CHR^{18}$ wherein R^{18} is optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, optionally substituted heterocyclyl or optionally substituted amino, or R^6 is hydrogen and R^7 is selected from alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl, or a group $-S(O)_mR^5$ as hereinbefore defined; and wherein R^3 and R^4 are independently selected from hydrogen, halogen, optionally substituted alkyl and optionally substituted cycloalkyl; and wherein A is an

optionally substituted N-linked nitrogen-containing five or six membered aromatic heterocyclic ring, provided that when X is $-CR^1$ and A represents a group of formula (IC)

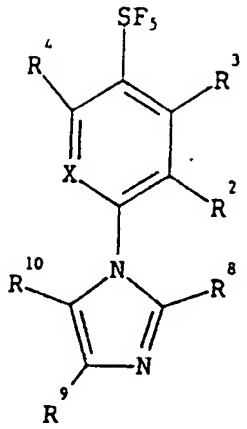


(IC)

wherein $R^{1'}$ is hydrogen, halogen, or a group $NR^{4'}R^{5'}$ wherein $R^{4'}$ and $R^{5'}$ are independently selected from hydrogen or alkyl; $R^{2'}$ is a group $-S(O)_{n'}R^{6'}$ wherein n' is 0, 1 or 2 and $R^{6'}$ is a haloalkyl group; and $R^{3'}$ is -CN or is a group CX' $-NY^{1'}Y^{2'}$ wherein X' is O or S or S=O; and $Y^{1'}$ and $Y^{2'}$ are independently selected from hydrogen, nitro, amino or alkyl optionally substituted by halogen, by cycloalkyl, by formyl, by C_{2-7} alkanoyl, by C_{4-7} cycloalkylcarbonyl, by C_{2-7} alkoxycarbonyl, by C_{2-7} haloalkoxycarbonyl, by an aryl group or by an aromatic heterocyclic group or
$Y^{1'}$ and $Y^{2'}$ together with the nitrogen to which they are attached form an aliphatic heterocyclic group containing from 4 to 8 atoms in the ring and optionally substituted by halogen or alkyl or
$Y^{1'}$ and $Y^{2'}$ together form the group $=CHY^3$ wherein Y^3 is alkyl, C_{2-6} alkenyl, aryl, an aromatic heterocycle, or amino optionally substituted by alkyl or
$Y^{1'}$ is hydrogen and $Y^{2'}$ is alkoxycarbonyl, alkylcarbonyl, optionally substituted aralkyl or a group $-S(O)_{n'}R^{6'}$ where $R^{6'}$ and n' are as hereinbefore defined, then R^1 and R^2 do not both represent halo.

3 A compound according to claim 2 wherein A is optionally substituted N-linked imidazole, optionally substituted N-linked pyrrole, optionally substitued N-linked pyrimidinone or optionally substituted N-linked pyridone.

4. A compound of formula (III)

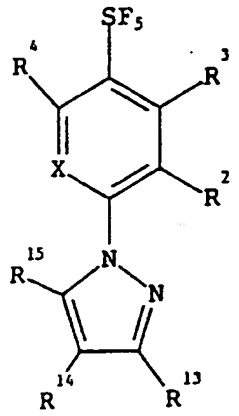


(III)

wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;
R^3 and R^4 are hydrogen;
R^8 is hydrogen, C_{1-4} alkyl optionally substitued by halogen, halogen, or a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen;
R^9 is hydrogen or C_{1-4} alkyl optionally substituted by halogen, or a group $-S(O)_mR^5$ as herein defined; and
R^{10} represents hydrogen or $-NR^1{}_1R^{12}$ wherein R^{11} and R^{12} are are independently selected from hydrogen and C_{1-4} alkyl.

5. A compound according to claim 4 wherein at least one of R^8, R^9 and R^{10} is other than hydrogen.

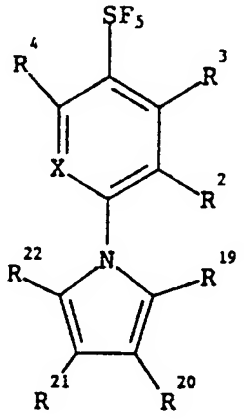
6. A compound of formula (IV)



(IV)

wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, and R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;
R^3 and R^4 are hydrogen;
R^{13} is cyano or a group $-C(Y)-NR^6R^7$ as herein defined;
R^{14} is a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen; and
R^{15} is C_{1-4} alkoxy, or a group $-S(O)_mR^5$ as herein defined.

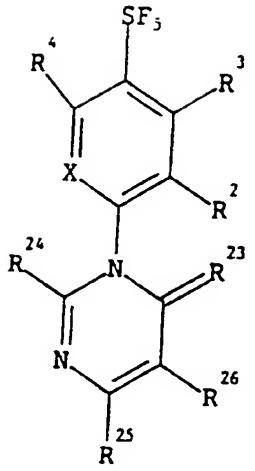
7. A compound of formula (V)



(V)

wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;
R^3 and R^4 are hydrogen;
and wherein R^{19} represents hydrogen, halogen, a group $-NR^{11}R^{12}$ wherein R^{11} and R^{12} independently represent hydrogen of C_{1-4} alkyl or a group $-S(O)_mR^5$ wherein m is 0, 1, or 2 and R^5 is C_{1-4} alkyl optionally substituted by halogen;
R^{20} is hydrogen or a group $-S(O)_mR^5$ as herein defined,
R^{21} represents cyano or a group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl; and
R^{22} represents hydrogen, halogen, a group $-S(O)_mR^5$ as herein defined.

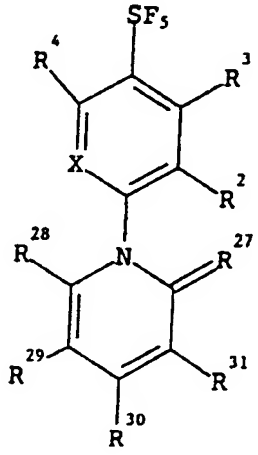
8. A compound of formula (VI)



(VI)

wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;
R^3 and R^4 are hydrogen;
R^{23} is oxygen or sulphur;
R^{24} is hydrogen,
R^{25} is C_{1-4} haloalkyl; and
R^{26} is hydrogen or C_{1-4} alkyl.

9. A compound of formula (VII)

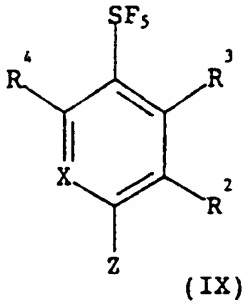


(VII)

wherein X is a group $-C(R_1)=$ wherein R_1 is halogen, R^2 is halogen, cyano or the group $-C(Y)-NR^6R^7$ wherein Y is =O or =S and R^6 and R^7 are independently selected from hydrogen or C_{1-4} alkyl;
R^3 and R^4 are hydrogen;

R^{28} is hydrogen;
R^{29} is hydrogen, halogen or C_{1-4} haloalkyl; R30 is hydrogen, or C_{1-4} haloalkyl; and R^{31} is hydrogen, halogen, nitro or cyano.

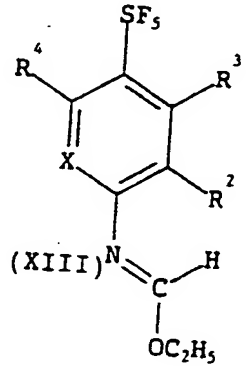
10. A method of preparing a compound of formula (II) as defined in claim 2 which comprises reacting a compound of formula (IX)



(IX)

wherein R^2, R^3 and R^4 are as defined in claim 2 and Z is halogen with a compound AH wherein A is as defined in claim 2 in the presence of a base and in a solvent.

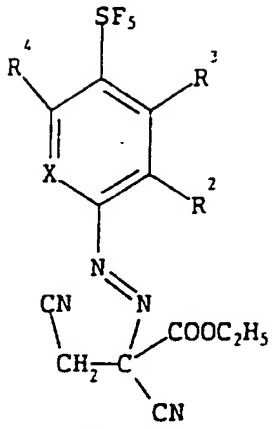
11. A compound of formula (XIII)



(XIII)

wherein R^2, R^3, R^4 and X are as defined in claim 2;

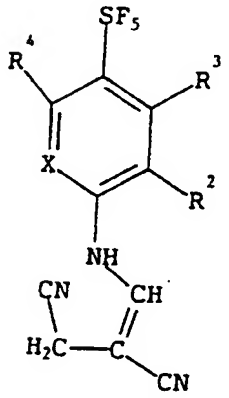
a compound of formula (XVII)



(XVII)

wherein R^2, R^3, R^4 and X are as defined in claim 2;

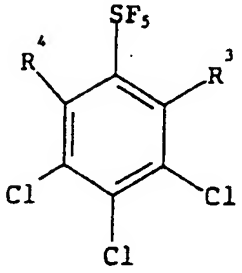
a compound of formula (XIX)



(XIX)

wherein R^2, R^3, R^4 and X are as defined in claim 2;

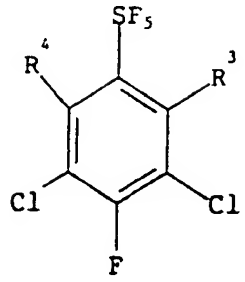
a compound of formula (XXIII)



(XXIII)

wherein R^3 and R^4 are as defined in claim 2;

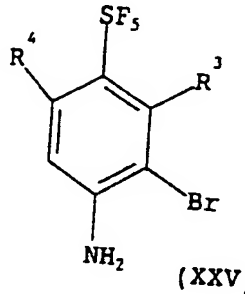
a compound of formula (XXIV)



(XXIV)

wherein R^3 and R^4 are as defined in claim 2;

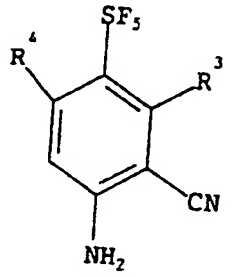
a compound of formula (XXV)



(XXV)

wherein R^3 and R^4 are as defined in claim 2;

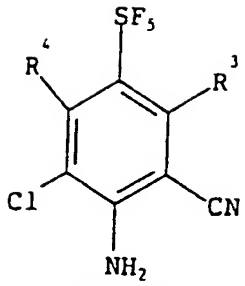
a compound of formula (XXVI)



(XXVI)

wherein R^3 and R^4 are as defined in claim 2;

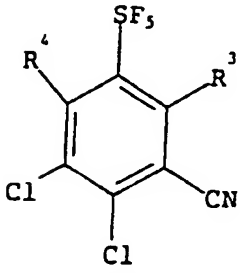
a compound of formula (XXVII)



(XXVII)

wherein R^3 and R^4 are as defined in claim 2;

a compound of formula (XXVIII)



(XXVIII)

wherein R^3 and R^4 are as defined in claim 2;

3,4,5-trichlorobenzenesulphurpentafluoride;
3,5-dichlorobenzenesulphurpentafluoride;
3,5-dichloro-4-fluorobenzenesulphurpentafluoride;
3-chloro-4,5-difluorobenzenesulphurpentafluoride;
4-amino-3-bromobenzenesulphurpentafluoride;
4-amino-3-cyanobenzenesulphurpentafluoride;
4-amino-3-chloro-5-cyanobenzenesulphurpentafluoride and
3-cyano-4,5-dichlorobenzenesulphurpentafluoride.

12. An insecticidal or acaricidal composition comprising an insecticidally or acaricidally effective amount of a compound according to any of claims 1 to 9 in association with an insecticidally or acaricidally inert dilutent or carrier.

13. A method of combating insect and acarine pests at a locus which comprises treating the locus with an insecticidally or acaricidally effective amount of a composition according to claim 12.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 94/00612

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07D207/36 C07D213/64 C07D231/28 C07D233/54 C07D239/36
A01N43/36 A01N43/40 A01N43/50 A01N43/54 A01N43/56
C07C381/00 C07D207/34 C07D233/84 C07D233/88 C07D521/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 396 427 (RHONE-POULENC AGROCHIMIE) 7 November 1990 cited in the application see the whole document; especially page 67, table 2, example 11 ---	1-5,12, 13
A	EP,A,0 403 309 (RHONE-POULENC AGRICULTURE LTD.) 19 December 1990 see the whole document; especially page 15, example 3, lines 51-52 ---	1,2,6, 12,13
A	EP,A,0 372 982 (RHONE-POULENC AGROCHIMIE) 13 June 1990 see the whole document; especially page 68, example 13 --- -/--	1-3,7, 12,13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
17 June 1994	27. 06. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Fink, D

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/GB 94/00612

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 338 686 (IMPERIAL CHEMICAL INDUSTRIES PLC) 25 October 1989 see the whole document; especially page 12, example 1 ---	1-3,8, 12,13
A	EP,A,0 216 541 (IMPERIAL CHEMICAL INDUSTRIES PLC) 1 April 1987 see the whole document; especially page 28, example 4(x) ---	1-3,9, 12,13
A	FR,A,2 255 296 (E.I. DU PONT DE NEMOURS AND COMPANY) 18 July 1975 see page 1, line 29 - page 2, line 20 see page 46, line 20 - line 22 ---	1-13
A	EP,A,0 398 499 (IMPERIAL CHEMICAL INDUSTRIES PLC) 22 November 1990 see page 33 - page 36; claims 1-7 see page 40; claims 21,22 ---	1-6,8,9, 12,13
P,X	WO,A,93 06089 (IMPERIAL CHEMICAL INDUSTRIES PLC) 1 April 1993 see page 25 - page 26; claims 1-6 see page 28; claims 9,10 -----	6,11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 94/00612

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0396427	07-11-90	AU-B-	640645	02-09-93
		AU-A-	5458990	08-11-90
		CA-A-	2015366	05-11-90
		CN-A-	1046898	14-11-90
		JP-A-	3027361	05-02-91
		OA-A-	9207	30-06-92
		US-A-	5223525	29-06-93
EP-A-0403309	19-12-90	AU-A-	5713190	20-12-90
		CA-A-	2018403	16-12-90
		CN-A-	1048035	26-12-90
		JP-A-	3109376	09-05-91
		OA-A-	9452	15-10-92
EP-A-0372982	13-06-90	AU-B-	641905	07-10-93
		AU-A-	4600089	21-06-90
		JP-A-	2243670	27-09-90
		OA-A-	9248	30-06-92
		PL-B-	162669	31-12-93
		TR-A-	25800	01-09-93
		US-A-	5187185	16-02-93
EP-A-0338686	25-10-89	AU-B-	618799	09-01-92
		AU-A-	3317989	26-10-89
		JP-A-	2006476	10-01-90
		US-A-	5077297	31-12-91
		US-A-	5149810	22-09-92
EP-A-0216541	01-04-87	AU-B-	614670	05-09-91
		AU-A-	4249889	05-04-90
		AU-B-	591704	14-12-89
		AU-A-	6259486	26-03-87
		CA-A-	1273937	11-09-90
		CA-A-	1278576	02-01-91
		CA-A-	1276182	13-11-90
		GB-A-	2183634	10-06-87
		JP-A-	62070362	31-03-87
		US-A-	4725607	16-02-88
FR-A-2255296	18-07-75	AU-B-	503626	13-09-79

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte nal Application No
PCT/GB 94/00612

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2255296		AU-A-	7643774	17-06-76
		CA-A-	1050972	20-03-79
		CH-A-	604507	15-09-78
		DE-A-	2460255	04-09-75
		GB-A-	1499512	01-02-78
		GB-A-	1499511	01-02-78
		JP-A-	50094127	26-07-75
		NL-A-	7416591	23-06-75
		US-A-	4069320	17-01-78
EP-A-0398499	22-11-90	AU-A-	5228290	25-10-90
		CN-A-	1046526	31-10-90
		JP-A-	3002160	08-01-91
		US-A-	5109004	28-04-92
WO-A-9306089	01-04-93	AU-A-	2541392	27-04-93

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number
WO 01/40195 A2

(51) International Patent Classification[7]: C07D 231/28, A61K 31/4152, 31/415

(21) International Application Number: PCT/EP00/12100

(22) International Filing Date: 1 December 2000 (01.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/168,658 2 December 1999 (02.12.1999) US

(71) Applicant: **AVENTIS CROPSCIENCE S.A.** [FR/FR]; 55, avenue René Cassin, F-69009 Lyon (FR).

(72) Inventors: **HUBER, Scot, Kevin**; 6104 Bramblewood Drive, Raleigh, NC 27612 (US). **CHOU, David, Teh-Wei**; 5120 Richland Drive, Raleigh, NC 27612 (US). **SCHNATTERER, Stefan**; Schillerring 10, 65795 Hattersheim (DE). **BASTIAANS, Henricus, Maria, Martinus**; Stockheimer Weg 9a, 61250 Usingen (DE).

(74) Agent: **RIPPEL, Hans, Christoph**; Aventis CropScience GmbH, Patent- und Lizenzabteilung, Industriepark Höchst, Gebäude K 801, 65926 Frankfurt (DE).

(81) Designated States *(national)*: AE, AG, AL, AM, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CN, CR, CU, CZ, DM, DZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KG, KP, KR, KZ, LC, LK, LR, LT, LV, MA, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, UZ, VN, YU, ZA.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *Without international search report and to be republished upon receipt of that report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/40195 A2

(54) Title: CONTROL OF ARTHROPODS IN ANIMALS

(57) Abstract: A method of controlling parasites in or on an animal comprising administering to the animal a parasiticidally effecive, substantially non-emetic 1-arylpyrazole.

Control of Arthropods in Animals

The present invention relates to a method of control of parasites in animals, compositions comprising a compound effective for the said control and compounds effective against parasites.

It is generally a goal of agronomists and veterinarians to possess sufficient means to control pests, particularly arthropods, when they attempt to invade or attack mammals, particularly domestic animals and/ or livestock. A classical method of controlling such pests has been the use of topical and/or systemic pesticides on or in the domestic animal which is being attacked. Generally effective treatments include the oral administration of insect growth regulators, such as lufenuron, or antihelminth compounds such as an ivermectin or an avermectin, or the topical application of the insecticide fipronil. It is advantageous to apply pesticides to animals in oral form so as to prevent the possible contamination of humans or the surrounding environment. It is an object of the present invention to provide new pesticides which may be used in domestic animals.

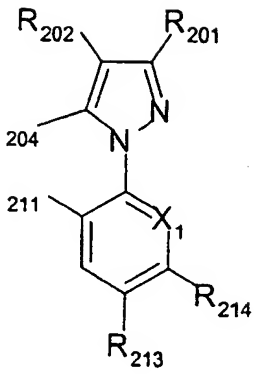
Another object of the invention is to provide safer pesticides for domestic animals.

Another object of the invention is to provide new pesticides for domestic animals that may be used in lower doses than existing pesticides.

These objects are met in whole or in part by the present invention.

US 5,079,370, EP-A 0,846,686, WO 98/24769 and WO 97/28126 disclose the use of arylpyrazoles as parasiticidal agents. However, these references are completely silent on the problem that anti parasitical agents often elicit emesis in the animal to be protected or cured from the parasites.

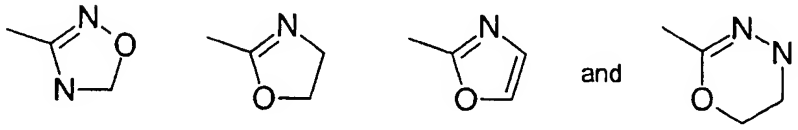
The present invention provides a method of controlling parasites in or on an animal comprising administering, preferably orally, to the animal a parasiticidally effective, substantially non-emetic amount of a 1-arylpyrazole of formula (I):



(I)

wherein:

R_{201} is cyano, C(O)alkyl, $C(S)NH_2$, $C(NH)OR_{203}$, $C(NH)SR_{203}$, alkyl, $C(=NOH)NH_2$, $C(=NNH_2)NH_2$, $C(O)NH_2$, $C(O)NHR_{205}$, $C(O)NR_{205}R_{206}$, haloalkyl or heterocyclyl from the group:



optionally substituted by R_{203};

R_{202} is $S(O)_hR_{203}$, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, cycloalkyl, halocycloalkyl, cycloalkyl-alkyl , C_2-C_6 alkynyl, nitro or imidazol-2-yl optionally substituted by alkyl, alkoxy, haloalkyl, halogen, cyano and/or nitro;

R_{203} is alkyl or haloalkyl;

R_{204} is -OH, $R_{205}O$-, HC(O)O-, $R_{205}C(O)O$-, $R_{205}OC(O)O$-, $NH_2C(O)O$-, $R_{205}NHC(O)O$-, $R_{205}R_{206}NC(O)O$-, $R_{205}S(O)_nC(O)O$-, $R_{206}SO_2O$-, aryl-SO_2O-, (C_4-C_7)-oxacycloalkyloxy, $R_{205}R_{206}N$-$C(NR_{205})$-O-, $R_{205}R_{206}N$-C(NH)-O- , $R_{205}NH$-$C(NR_{205})$-O-, $R_{205}NH$-C(NH)-O-, $R_{205}N$=CH-O-, $R_{205}N=C(R_{206})$-O-, $R_{205}NH$-C(S)-O-, $R_{205}R_{206}N$-C(S)-O- ;

R_{205} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, adamantyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, haloalkylaminoalkyl, di(haloalkyl)aminoalkyl, aryl optionally substituted, hetaryl optionally substituted,

arylalkyl optionally substituted, hetarylalkyl optionally substituted, C_2-C_6 alkenyl, C_2-C_6 alkinyl;

R_{206} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, aryl optionally substituted, hetaryl optionally substituted, arylalkyl optionally substituted, hetarylalkyl optionally substituted;

or R_{205} and R_{206} may form together with the nitrogen to which they are attached a 3 to 7 membered ring which additionally may contain one or more heteroatoms selected from nitrogen, oxygen and sulfur;

X_1 is selected from nitrogen and C-R_{212};

R_{211}, R_{212} are independently selected from halogen, hydrogen, CN, C_1-C_3 alkyl and NO_2;

R_{213} is selected from halogen, haloalkyl, haloalkoxy, -$S(O)_kCF_3$, and $-SF_5$ or forms a ring with R_{214};

R_{214} is hydrogen or may constitute together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring;

and

h, k and n are independently selected from 0, 1, and 2;

and veterinarily acceptable salts thereof.

By the term "veterinarily acceptable salts" is meant salts the anions of which are known and accepted in the art for the formation of salts for veterinary use. Suitable acid addition salts, e.g. formed by compounds of formula (I) containing a basic nitrogen atom, e.g. an amino group, include salts with inorganic acids, for example hydrochlorides, sulphates, phosphates and nitrates and salts with organic acids for example acetic acid.

When R_{204} is OH the pyrazole structure can also be exhibited by its tautomeric form as pyrazolon structure.

Unless otherwise specified, alkyl and alkoxy groups are straight chain or branched and are generally lower alkyl and alkoxy groups, that is having from one to six carbon atoms, preferably from one to four carbon atoms. Generally, the haloalkyl,

haloalkoxy and haloalkylamino groups have from one to four carbon atoms. Halogen means F, Cl, Br, and I, preferably F and Cl. The haloalkyl and haloalkoxy and haloalkylamino groups can bear one or more halogen atoms; preferred groups of this type include $-CF_3$ and $-OCF_3$. Cycloalkyl groups generally have from 3 to 6 carbon atoms, preferably from 3 to 5 carbon atoms and may be substituted by one or more halogen atoms. Preferably in compounds of formula (I), alkyl groups are generally substituted by from one to five halogen atoms, preferably from one to three halogen atoms. Chlorine and fluorine atoms are preferred.

In compounds of formula (I) the following examples of radicals are provided:

An example of cycloalkylalkyl is cyclopropylmethyl;

an example of cycloalkoxy is cyclopropyloxy;and

an example of alkoxyalkyl is CH_3OCH_2-.

Generally, in dialkylamino or di(haloalkyl)amino radicals, the alkyl and haloalkyl groups on nitrogen may be chosen independently of one another.

Generally, the term "aryl" means a carbocyclic aromatic radical having preferably 6 to 14, in particular 6 to 12, carbon atoms, for example phenyl, naphthyl or biphenylyl, preferably phenyl;

the term "heterocyclyl" preferably a hetaryl or heteroaliphatic ring system, "hetaryl" preferably being understood as meaning an aryl radical in which at least one CH group is replaced by N and/or at least two adjacent CH groups are replaced by S, NH or O, for example a radical of thiophene, furan, pyrrole, thiazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, pyrazine, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or 4H-quinolizine;

and the term "heteroaliphatic ring system" preferably a (C_3-C_8)cycloalkyl radical in which at least one carbon unit is replaced by O, S or a group NR' and R' is hydrogen, (C_1-C_4)alkyl, (C_1-C_4)alkanoyl, (C_1-C_4)alkoxycarbonyl, (C_1-C_4)alkylsulfonyl, (C_1-C_4)alkoxy or aryl;

The substituents with which the various aliphatic, cycloaliphatic, aromatic and heterocyclic ring systems can be provided are, for example, halogen, nitro, cyano, di-(C_1-C_4)alkylamino, (C_1-C_4)alkyl, (C_3-C_8)cycloalkyl, (C_1-C_4)trialkylsilyl, (C_1-C_4)alkoxy, (C_1-C_4)alkoxy-(C_1-C_4)alkyl, (C_1-C_2)alkoxy-$[CH_2CH_2O]_{0,1,2}$-ethoxy, (C_1-C_4)alkylthio, (C_1-C_4)alkylsulfinyl, (C_1-C_4)alkylsulfonyl, phenyl, benzyl, phenoxy, halophenoxy, (C_1-C_4)alkylphenoxy, (C_1-C_4)alkoxyphenoxy, phenylthio, heterocyclyl, heterocyclylthio or heterocyclyloxy, it being possible for one or more, in the case of fluorine also up to the maximum number of, hydrogen atoms in the alkyl radicals and the radicals derived therefrom to be replaced by halogen, preferably chlorine or fluorine, where, in the event that these substituents are (C_1-C_4)alkyl, they may also be linked cyclically and where one or two aliphatic carbon units in these fused ring systems, such as, for example, the indane, di-, tetra- or decahydronaphthyl or benzocycloheptane system, may be replaced by heteroatom units such as oxygen or sulfur and where one or more, in the case of fluorine also up to the maximum number of, hydrogen atoms on the aliphatic carbon atom units can be replaced by halogen or (C_1-C_4)alkyl.

It is also to be understood that enantiomeric and diastereomeric forms of the compounds of formulae (I) and salts thereof are embraced by the present invention.

By the term non-emetic is meant a compound that does not generally elicit emesis from the animal when a protective, preventative or cleaning dose is administered to the animal. By the term emesis is meant vomiting. Generally an emetic substance elicits the said emesis in less than 24 hours after administration, preferably less than 8 hours, more preferably less than 2 hours. Generally when the compounds of the invention are administered to a population of animals, more than 70% of the animals are free of emesis, preferably more than 80%, most preferably more than 90%.

Preferred compounds of the formula (I) are those wherein:

R_{201} is cyano, C(O)alkyl, $C(S)NH_2$, alkyl, $C(=NOH)NH_2$ or $C(=NNH_2)NH_2$;
R_{202} is $S(O)_hR_{203}$, C_2-C_3 alkenyl, C_2-C_3 haloalkenyl, cycloalkyl, halocycloalkyl, cycloalkyl-alkyl , C_2-C_3 alkynyl;
R_{203} is alkyl or haloalkyl;
R_{204} is -OH, $R_{205}O$-, HC(O)O-, $R_{205}C(O)O$-, $R_{205}OC(O)O$-, $NH_2C(O)O$-, $R_{205}NHC(O)O$-, $R_{205}R_{206}NC(O)O$-, $R_{205}S(O)_nC(O)O$-;
R_{205} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, haloalkylaminoalkyl, di(haloalkyl)aminoalkyl,
R_{206} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl,
or R_{205} and R_{206} may form together with the nitrogen to which they are attached a 3 to 7 membered ring which additionally may contain one or more heteroatoms selected from nitrogen, oxygen and sulfur;
X_1 is selected from nitrogen and C-R_{212};
R_{211}, R_{212} are independently selected from halogen, hydrogen, CN, and NO_2;
R_{213} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_kCF_3$, and $-SF_5$
R_{214} is hydrogen;
and
h, k and n are independently selected from 0, 1, and 2.

Further compounds of formula (I) which are preferred according to the present invention are those wherein:
R_{201} is cyano;
R_{202} is $S(O)_hR_{203}$;
R_{203} is alkyl or haloalkyl;
R_{204} is OH or $R_{205}O$;
X_1 is selected from nitrogen and C-R_{212};
R_{211} and R_{212} are independently selected from halogen, hydrogen, CN and NO_2;
R_{213} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_kCF_3$, and $-SF_5$; and

h and k are independently selected from 0, 1, and 2.

The compounds of formula (I) of the present invention preferably have one or more of the following features:

R_{201} is cyano;

R_{203} is halomethyl, preferably CF_3;

R_{211} and R_{212} are independently halogen;

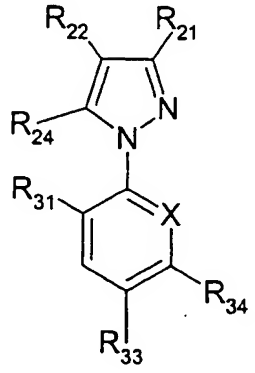
X_1 is C-R_{212};

R_{213} is haloalkyl, haloalkoxy or $-SF_5$; or

h is 0 or 1, or 2.

A further embodiment of the invention includes compounds of the formula (I), with the proviso that if R_{201} is CN and R_{202} is $S(O)_hR_{203}$ then R_{204} is not $R_{205}O$ or $R_{205}R_{206}N$-C(O)-O-.

In another aspect of the present invention there is provided a method of controlling parasites in or on an animal by administering to the animal an 1-arylpyrazole of formula (II):



(II)

wherein:

R_{21} is cyano, $C(=S)NH_2$, $C(=NOH)NH_2$ or $C(=NNH_2)NH_2$;

R_{22} is $S(O)_mR_{23}$;

R_{23} is alkyl or haloalkyl;

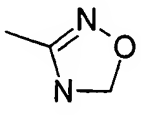
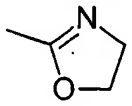
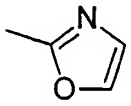
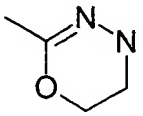
R_{24} is OH, HC(O)O-, $R_{25}C(O)O$-, $R_{25}OC(O)O$-, $R_{25}R_{25}$-N-C(O)-O- or $R_{25}S(O)_nC(O)O$-;
R_{25} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, adamantyl, adamantyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, haloalkylaminoalkyl, di(haloalkyl)aminoalkyl, aryl optionally substituted, hetaryl optionally substituted, arylalkyl optionally substituted, hetarylalkyl optionally substituted, C_2-C_6 alkenyl, C_2-C_6 alkinyl;
or two groups R_{25} may form together with the nitrogen to which they are attached a 3 to 7 membered ring which additionally may contain one or more heteroatoms selected from nitrogen, oxygen and sulfur;
X is selected from nitrogen and C-R_{32};
R_{31} and R_{32} are independently selected from halogen, hydrogen, CN, C_1-C_3 alkyl and NO_2;
R_{33} is selected from halogen, haloalkyl, haloalkoxy, -$S(O)_rCF_3$, and $-SF_5$ or forms a ring together with R_{34} ;
R_{34} is hydrogen or may constitute together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring;
m is 0, 1 or 2;
r is selected from 0, 1, and 2;
and veterinarily acceptable salts thereof;
provided that if R_{21} is cyano then R_{24} is not $R_{25}R_{25}$-N-C(O)-O-.
Preferred are compounds of formula (II),
wherein:
R_{21} is cyano, $C(=S)NH_2$, $C(=NOH)NH_2$ or $C(=NNH_2)NH_2$;
R_{22} is $S(O)_mR_{23}$;
R_{23} is alkyl or haloalkyl;
R_{24} is OH, HC(O)O-, $R_{25}C(O)O$-, $R_{25}OC(O)O$- or $R_{25}S(O)_nC(O)O$-;
R_{25} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl;
X is selected from nitrogen and C-R_{32};
R_{31} and R_{32} are independently selected from halogen, hydrogen, CN, C_1-C_3 alkyl and NO_2;

R_{33} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_rCF_3$, and $-SF_5$

In another aspect of the present invention there is provided a compound of formula (II) or salt thereof as hereinbefore described with the proviso that the compound is not 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylthio-5-hydroxypyrazole.

A further preferred class of compounds of formula (II) are those wherein:
R_{21} is cyano;
R_{22} is $S(O)_mR_{23}$;
R_{23} is haloalkyl, preferably CF_3;
R_{24} is OH;
X is selected from nitrogen and $C\text{-}R_{32}$;
R_{31} and R_{32} are independently selected from halogen,
R_{33} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_rCF_3$, and $-SF_5$;
m and r are independently selected from 0, 1, and 2
with the proviso that the compound is not 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylthio-5-hydroxypyrazole.

In a further aspect of the invention the following groups of compounds are provided:
Compounds of the formula (I), wherein
R_{201} is $C(O)NH_2$, $C(O)NHR_{205}$, $C(O)NR_{205}R_{206}$, $C(O)N{=}S(R_{203})_2$, haloalkyl or heterocyclyl from the group:




and


optionally substituted by R_{203}.

Compounds of the formula (I), wherein

R_{202} is nitro or imidazol-2-yl optionally substituted by alkyl, alkoxy, haloalkyl, halogen, cyano, nitro.

Compounds of the formula (I), wherein
R_{204} is $R_{206}SO_2O$-, aryl-SO_2O-, (C_4-C_7)-oxacycloalkyloxy, $R_{205}R_{206}N$-$C(NR_{205})$-O-, $R_{205}R_{206}N$-C(NH)-O- , $R_{205}NH$-$C(NR_{205})$-O-, $R_{205}NH$-C(NH)-O-, $R_{205}N$=CH-O-, $R_{205}N$=$C(R_{206})$-O-, $R_{205}NH$-C(S)-O-, $R_{205}R_{206}N$-C(S)-O-.

Compounds of the formula (I), wherein
R_{214} constitute together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring.

The compounds 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfinyl-5-hydroxypyrazole and 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfonyl-5-hydroxypyrazole are highly preferred compounds according to the invention.

The following compounds of formula (I) are preferred according to the present invention as listed in Tables 1 to 3. The Compound Numbers are for identification purposes only. The following symbols are hereby defined: Me means methyl; Et means ethyl; n-Pr means n-propyl; i-Pr means isopropyl; n-Bu means n-Butyl; and Ph means Phenyl.

Table 1

Compounds of formula (I) wherein R_{201} is cyano; R_{202} is SCF_3; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and $R_{213}$is CF_3 or SF_5.

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound Number (R_{213}= CF_3)	Compound Number (R_{213}=SF_5)	R_{204}	Phys. data
1-1	1-2	OH	19F: -44.9 -63.8 ppm
2-1	2-2	OMe	mp. 83
3-1	3-2	OEt	mp. 105
4-1	4-2	OPr	
5-1	5-2	O-i-Pr	
6-1	6-2	O-n-Bu	
7-1	7-2	OCH_2OMe	
8-1	8-2	OCH_2CH_2OMe	
9-1	9-2	OCH_2OEt	
10-1	10-2	OCH_2CH_2OEt	
11-1	11-2	OC(O)Me	
12-1	12-2	OC(O)Et	
13-1	13-2	OC(O)n-Pr	
14-1	14-2	OC(O)H	
15-1	15-2	$OC(O)NH_2$	
16-1	16-2	OC(O)NHMe	
17-1	17-2	OC(O)NHEt	
18-1	18-2	OC(O)NHnPr	
19-1	19-2	$OC(O)NMe_2$	mp. 126

Table 2

Compounds of formula (I) wherein R_{201} is cyano; R_{202} is $SOCF_3$; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 or SF_5.

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound Number (R_{213}= CF_3)	Compound Number (R_{213}=SF_5)	R_{204}	Phys. data
1-3	1-4	OH	mp. 185
2-3	2-4	OMe	mp. 136
3-3	3-4	OEt	mp. 157
4-3	4-4	OPr	
5-3	5-4	O-i-Pr	
6-3	6-4	O-n-Bu	
7-3	7-4	OCH_2OMe	
8-3	8-4	OCH_2CH_2OMe	
9-3	9-4	OCH_2OEt	
10-3	10-4	OCH_2CH_2OEt	
11-3	11-4	ONa	19F: -60.9 -72.6
12-3	12-4	OC(O)Et	
13-3	13-4	OC(O)n-Pr	
14-3	14-4	OC(O)H	
15-3	15-4	$OC(O)NH_2$	
16-3	16-4	OC(O)NHMe	
17-3	17-4	OC(O)NHEt	
18-3	18-4	OC(O)NHnPr	
19-3	19-4	$OC(O)NMe_2$	

Table 3

Compounds of formula (I) wherein R_{201} is cyano; R_{202} is SO_2CF_3; R_{211} is Cl; X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 or SF_5.

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound Number (R_{213}= CF_3)	Compound Number (R_{213}=SF_5)	R_{204}	Phys. data
1-5	1-6	OH	19F: -63.8 -79.9 ppm
2-5	2-6	OMe	mp. 151
3-5	3-6	OEt	mp. 132
4-5	4-6	OPr	
5-5	5-6	O-i-Pr	
6-5	6-6	O-n-Bu	
7-5	7-6	OCH_2OMe	
8-5	8-6	OCH_2CH_2OMe	
9-5	9-6	OCH_2OEt	
10-5	10-6	OCH_2CH_2OEt	
11-5	11-6	OC(O)Me	
12-5	12-6	OC(O)Et	
13-5	13-6	OC(O)n-Pr	
14-5	14-6	OC(O)H	
15-5	15-6	$OC(O)NH_2$	
16-5	16-6	OC(O)NHMe	
17-5	17-6	OC(O)NHEt	
18-5	18-6	OC(O)NHnPr	
19-5	19-6	$OC(O)NMe_2$	

Table 4

Compounds of formula (I) wherein R_{201} is alkyl or haloalkyl; R_{202} is SO_nR_{203}; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 ;

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{201}	R_{202}	R_{204}	Phys.Data
1-7	CH_3	SCF_3	OH	19F: -45.9 -63.5 ppm
2-7	CH_3	$SOCF_3$	OH	
3-7	CH_3	SO_2CF_3	OH	
4-7	CH_3	$SCClF_2$	OH	19F: -30.4 -63.7 ppm
5-7	CH_3	$SOCClF_2$	OH	
6-7	CH_3	SO_2CClF_2	OH	
7-7	CH_3	$SCCl_2F$	OH	
8-7	CH_3	$SOCCl_2F$	OH	
9-7	CH_3	SC_2F_5	OH	
10-7	CH_3	SC_2H_5	OH	
11-7	CH_3	SCF_3	OMe	
12-7	CH_3	SCF_3	OEt	
13-7	CH_3	SMe	OH	
14-7	C_2H_5	SCF_3	OH	
15-7	CF_3	SCF_3	OH	
16-7	CHF_2	SCF_3	OH	
17-7	CF_3	$SOCF_3$	OH	
18-7	CF_3	SO_2CF_3	OH	
19-7	CF_3	$SCClF_2$	OH	
20-7	CF_3	$SCCl_2F$	OH	

Table 5

Compounds of formula (I) wherein R_{202} is SO_hR_{203}; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 ;

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{201}	R_{202}	R_{204}	Phys. data
1-8	$CONH_2$	SCF_3	OH	mp. 197
2-8	$CONH_2$	$SOCF_3$	OH	
3-8	$CONH_2$	SO_2CF_3	OH	
4-8	$CSNH_2$	SCF_3	OH	mp. 150
5-8	$CSNH_2$	$SOCF_3$	OH	
6-8	$CSNH_2$	SO_2CF_3	OH	
7-8	$CONMe_2$	SCF_3	OH	
8-8	$C(NOH)NH_2$	$SCClF_2$	OH	mp. 156
9-8	$C(NOH)NH_2$	SCF_3	OH	mp. 184
10-8	$COCH_3$	SCF_3	OH	19F: -44.5 -61.7
11-8	$COCH_3$	$SCClF_2$	OH	19F: -29.4 -61.0
12-8	$CONH_2$	SCF_3	OEt	
13-8	$CONH_2$	$SCClF_2$	OEt	
14-8	Oxadiazolin-3-yl	SCF_3	OH	
15-8	Oxazolin-2-yl	SCF_3	OH	
16-8	$CON=S(iPr_2)$	SCF_3	OH	
17-8	$CON=S(iPr)_2$	$SOCF_3$	OH	
18-8	$CON=S(iPr)_2$	$SO2CF_3$	OH	
19-8	$CONH_2$	SCF_3	OMe	mp. 148-151
20-8				

Table 6

Compounds of formula (I) wherein R_{201} is CN; R_{202} is SO_hR_{203}; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 ;

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{202}	R_{204}	Phys. data
1-9	$SCClF_2$	OH	19F: -30.7 -63.7
2-9	$SOCClF_2$	OH	
3-9	SO_2CClF_2	OH	
4-9	$SCCl_2F$	OH	
5-9	$SOCCl_2F$	OH	
6-9	SO_2CCl_2F	OH	
7-9	SC_2F_5	OH	
8-9	SCH_2CF_3	OH	
9-9	$SCCl_2CF_3$	OH	
10-9	$SCCl_2CH_3$	OH	
11-9	SC_2H_5	OH	1H: 1.25,3H; 2.71,3H; 7.72,2H;
12-9	$SCHF_2$	OH	
13-9	$SCClF_2$	OEt	mp. 91
14-9	$SOCClF_2$	OEt	mp. 161
15-9	$SCClF_2$	$OCONMe_2$	
16-9	$SCClF_2$	OCOtBu	
17-9	SCH_3	OH	mp. 66
18-9	SCH_3	$OCONMe_2$	1H: 2.43,3H; 2.96,6H;7.75,2H;
19-9	$SCBrF_2$	OH	
20-9	$SCCl_3$	OH	
21-9	$SCCl_2F$	OMe	mp. 154
22-9	$SOCCl_2F$	OMe	mp. 136
23-9	SO_2CCl_2F	OMe	mp. 189
24-9	SO_2CClF_2	OEt	mp. 130
25-9	$SCClF_2$	OMe	mp. 87
26-9	$SOCClF^2$	OMe	mp. 139
27-9	SO^2CClF^2	OMe	mp. 166

Table 7

Compounds of formula (I) wherein R_{201} is CN; R_{202} is SO_nR_{203}; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 ;

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{202}	R_{204}		Phys. data
1-10	SCF_3	OCH_2-CCH		19F: -44.6 -63.8
2-10	SCF_3	OCH_2COOEt		mp. 71
3-10	SCF_3	OCOtBu		mp. 82
4-10	SCF_3	OCO-Ph-4-OMe		19F: -43.5 -63.9
5-10	SCF_3	OSO_2Me		mp. 110
6-10	SCF_3	OCO-Pyrrolidin		mp. 101
7-10	SCF_3	OCO-Morpholin		19F: -43.5 -63.8
8-10	SCF_3	OCO-N(i-Pr)$_2$		mp. 120
9-10	SCF_3	$OCO-NPh_2$		mp. 142
10-10	SCF_3	OCO-N(Me)Ph		19F: -43.6 -63.7
11-10	SCF_3	OCO-Carbazol		mp. 148
12-10	SCF_3	OCO-Adamantyl		mp. 142
13-10	SCF3	OCO-Mesityl		mp. 103
14-10	SCF3	OCH_2Ph		mp. 73
15-10	SCF3	OSO_2-4-Tolyl		
16-10	SCF3	O-C(NMe)Nme_2		
17-10	SCF3	O-CH=NC_2H_4OEt		
18-10	SCF3	OCH_2CONH_2		mp. 156
19-10	SCF3	O-C(N(i-Pr))NHiPr		
20-10	SCF3	O-C(S)-NHEt		

Table 8

Compounds of formula (I) wherein R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is CF_3 ; Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{201}	R_{202}	R_{204}	Phys. data
1-11	CN	4,5-Dicyano-imidazol-2-yl	OH	
2-11	CN	4,5-Dicyano-imidazol-2-yl	OEt	
3-11	CH_3	4,5-Dicyano-imidazol-2-yl	OH	
4-11	CH_3	4,5-Dicyano-imidazol-2-yl	OEt	1H: 1.28, 3H; 2.55, 3H; 4.08, 2H; 7.77, 2H;
5-11	CN	$-CH=CCl_2$	OEt	
6-11	CN	$-CH_2CH=CH_2$	OAllyl	mp. 62-66
7-11	CN	$-CH=CBr_2$	OEt	
8-11	CN	Cyclopropyl	OEt	
9-11	CN	$c\text{-}C_6H_{11}$	OEt	
10-11	CN	NO_2	OH	mp. 107
11-11	CN	NO_2	OEt	
12-11	CN	-CC-Me	OEt	
13-11	CN	$-CC\text{-}SiMe_3$	OEt	

Table 9

Compounds of formula (I) wherein R_{201} is CN; R_{202} is SO_nR_{203}; R_{211} is Cl, R_{214} and R_{213} form the unit CF_2OCF_2;

Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{202}	R_{204}	$X=CR_{212}$	Phys. data
1-12	SCF_3	OH	CH	
2-12	SCF_3	OH	C-Cl	
3-12	SCF_3	OEt	C-Cl	
4-12	$SOCF_3$	OH	CH	
5-12	$SOCF_3$	OH	C-Cl	
6-12	SO_2CF_3	OH	CH	
7-12	SO_2CF_3	OH	C-Cl	
8-12	$SCClF_2$	OH	C-Cl	
9-12	$SCCl_2F$	OH	C-Cl	
10-12	SC_2H_5	OH	C-Cl	

Table 10

Compounds of formula (I) wherein R_{201} is CN; R_{202} is SO_nR_{203}; R_{211} is Cl, X_1 is C-Cl, R_{214} is H and R_{213} is OCF_3 ;

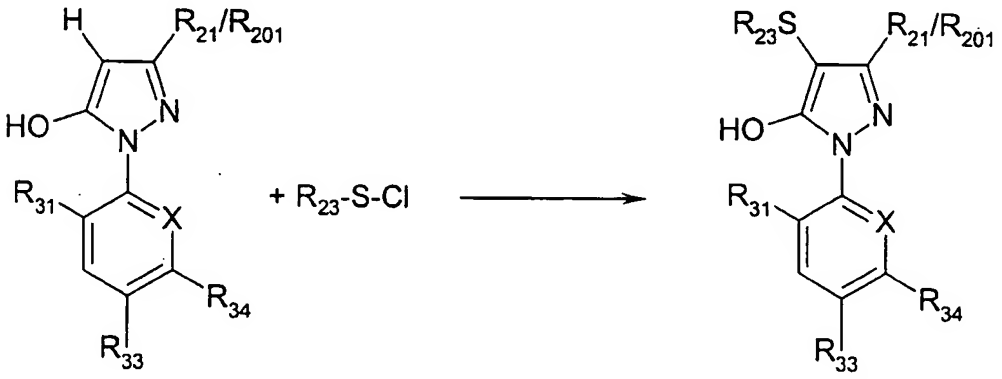
Phys. data: melting point (°C) or NMR (^1H, ^{19}F-NMR, ppm)

Compound No	R_{202}	R_{204}	Phys data
1-13	SCF_3	OH	
2-13	$SOCF_3$	OH	
3-13	SO_2CF_3	OH	
4-13	SCF_3	OMe	mp. 101
5-13	$SOCF_3$	OMe	mp. 104
6-13	SO_2CF_3	OMe	mp. 117
7-13	$SCCl_2F$	OMe	mp. 123
8-13	SCF_3	OEt	
9-13	$SOCF_3$	OEt	
10-13	SO_2CF_3	OEt	

Methods of Synthesis

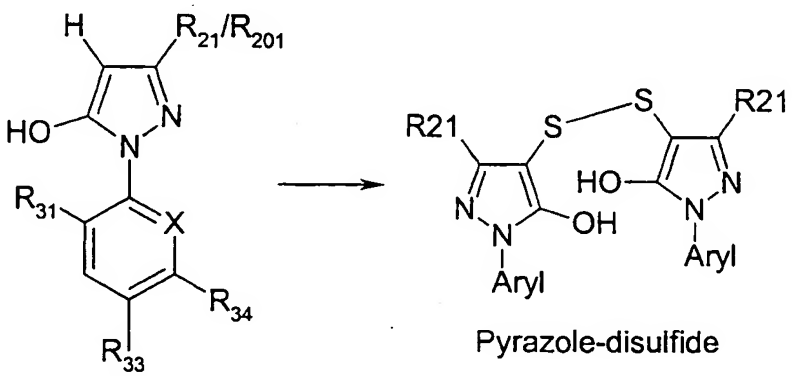
Method 1

The compounds of formula (I) and (II) with R_{204}/R_{24} = OH and R_{22}= SR_{23} can be synthesized by reacting 5-hydroxypyrazoles with sulfenylchlorides with or without bases in organic solvents (see e.g. EP-A-295 117):

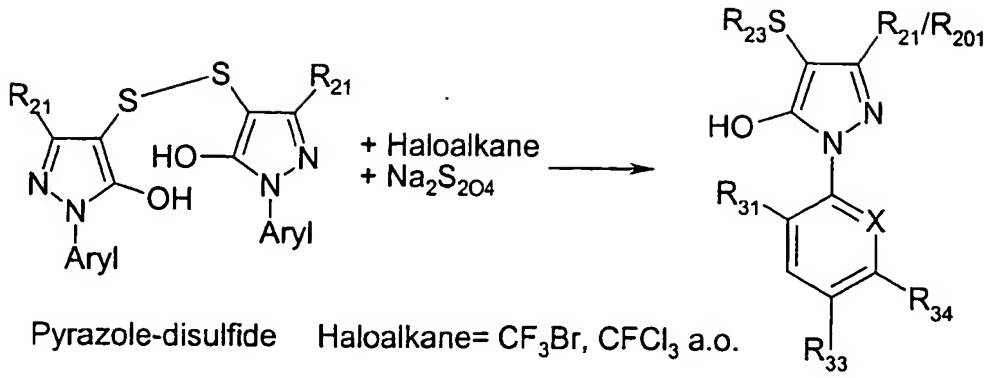


Method 2

The compounds of formula (I) and (II) with R_{204}/R_{24} = OH and R_{22}= SR_{23} can be synthesized by reacting 5-hydroxypyrazoles with disulfurdichloride. The resulting pyrazoledisulfides can be alkylated to yield 4-pyrazolsulfides (see e.g. EP-A-374 061, EP295117, C. Wakselman, J. Chem. Soc. Perkin Trans 1, 1992 3371-3375) :



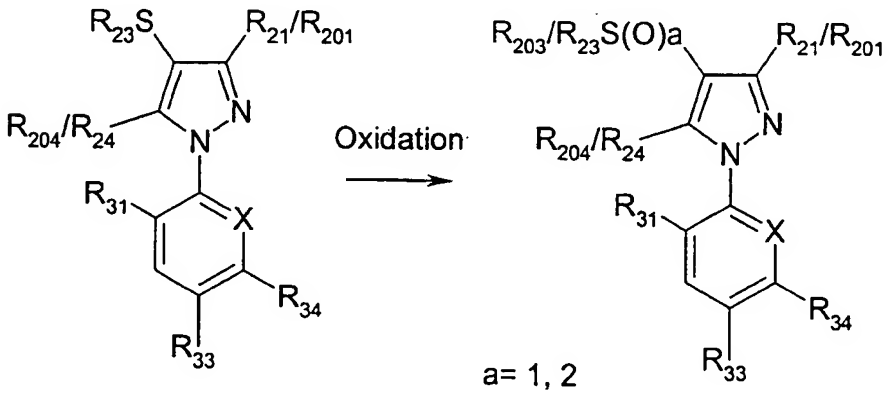
Pyrazole-disulfide



Pyrazole-disulfide Haloalkane= CF_3Br, $CFCl_3$ a.o.

Method 3

The compounds of formula (I) and (II) with R_{204}/R_{24} = OH and R_{22}= $S(O)_aR_{23}$ (a=1,2) can be synthesized by reacting pyrazolsulfides R_{22}= SR_{23} with oxidizing agents like peroxy compounds (hydrogenperoxide, organic peroxides as peroxyaceticacid), halogenderivatives (like periodate salts) and others to obtain sulfoxides R_{22}= SOR_{23} and sulfones R_{22}=SO_2R_{23} (see e.g. EP-A-295 117).



In another aspect of the present invention, compounds of formula (II) wherein R_{24} is HC(O)O-, $R_{25}C(O)O$-, $R_{25}OC(O)O$-, or $R_{25}S(O)_nC(O)O$ and R_{21}, R_{22}, R_{31}, R_{33}, X and n are defined above are generally prepared by reaction of compounds of formula (II) wherein R_{24} is OH and R_{21}, R_{22}, R_{31}, R_{33}, X and n are defined above with a

compounds of formulae (III), (IV), (V), and (VI) respectively wherein X_2 is a leaving group such as a halogen atom or an acetyl group:

$HC(O)X_2$ (III) $R_{25}C(O)X_2$ (IV) $R_{25}OC(O)X_2$ (V) $R_{25}S(O)_nC(O)X_2$ (VI)

Compounds of general formula (II) wherein of formula (II) wherein R_{24} is OH and R_{21}, R_{22}, R_{31}, R_{33}, X and n are defined above may be prepared by methods known in the art generally or by methods described in International Patent Publications WO 94/21606, WO 97/07102, WO 98/24767, WO 98/28277, WO 98/28278 and WO 98/28279, European Patent Application 385809, and United States Patent 5232940, 5047550 or other methods known to the person skilled in the art.

The present invention also relates to a composition comprising a parasiticidally effective, substantially non-emetic amount of a compound of formula (I) or a salt thereof and an acceptable carrier. Acceptable carriers for the use of the compounds are generally known to the skilled addressee concerned with pest control in animals, particularly domestic animals, most preferably dogs or cats.

The compositions which can be used in the invention can comprise generally from about 0.001 to 95% of the compound of formula (I) or a salt thereof. The remainder of the composition up to 100% comprises a carrier as well as generally various additives. In this specification and the accompanying claims, percentages are by weight.

The diluted liquid formulations generally comprise from about 0.001 to about 3% of compound of formula (I) or a salt thereof, preferably from about 0.1 to about 0.5%. Solid formulations generally comprise from about 0.1 to about 8% of compound of formula (I) or a salt thereof, preferably from about 0.5 to about 1.5%.

Compositions for oral administration comprise one or more of the compounds of general formula (I) or salts thereof in association with veterinarily acceptable carriers or coatings and include, for example, tablets, pills, capsules, gels, drenches, medicated feeds, medicated drinking water, medicated dietary supplements, slow-

release boluses or other slow-release devices intended to be retained within the gastro-intestinal tract. Any of these may incorporate the active ingredients contained within micro-capsules or coated with acid-labile or alkali-labile or other pharmaceutically acceptable enteric coatings. Feed premixes or concentrates containing compounds of the present invention for use in preparation of medicated diets, drinking water or other materials for consumption by animals may also be used. In a highly preferred embodiment, the compositions are administered postprandially, preferably from just after a meal to 2 hours after the meal.

In a highly preferred embodiment, there is provided a product which is readily chewed by the animal and which product does generally not allow human contamination when the product is provided to the animal by hand.

The compounds of general formula (I) or salts thereof may be administered before, during or after meals. The compounds of general formula (I) or salts thereof may be mixed with a carrier and/or a foodstuff.

According to the present invention the compound of formula (I) or a salt thereof is administered orally in a dose to the animal in a dose range generally from 0.1 to 500 mg/kg of the compound of formula (I) or a salt thereof per kilogram of animal body weight (mg/kg), preferably from 1 to 100 mg/kg, more preferably from 1 to 50 mg/kg, even more preferably from 2 to 25 mg/kg, most preferably from 3 to 15 mg/kg

According to the present invention, the frequency of treatment of the animal, preferably the domestic animal to be treated by the compound of formula (I) or a salt thereof is generally from about once per week to about once per year, preferably from about once every two weeks to about once every six months, more preferably from about once every two weeks to once every three months, and most preferably from about once every two weeks to about once every six weeks.

Generally the animal to be treated is a domestic animal, preferably a domestic companion animal. More preferably the animal to be treated is a dog and/or a cat.

Accordingly, in a preferred embodiment there is provided a method of controlling parasites in or on a cat comprising administering orally to the cat a parasitically effective, substantially non emetic amount of a 1-arylpyrazole of formula (I).

In a further preferred embodiment there is provided a method of controlling parasites in or on a dog comprising administering orally to the dog a parasitically effective, substantially non emetic amount of a 1-arylpyrazole of formula (I).

The present invention also relates to a composition comprising a parasiticidally effective amount of a compound of formula (II) or a salt thereof and an acceptable carrier. Acceptable carriers for the use of the compounds are generally known to the skilled addressee concerned with pest control in animals, particularly domestic animals, most preferably dogs or cats.

In another aspect of the present invention, the compounds of formula (II) or salts thereof may be used in the field of veterinary medicine or livestock husbandry or in the maintenance of public health against arthropods, helminths or protozoa which are parasitic internally or externally upon vertebrates, particularly warm-blooded vertebrates, for example domestic animals, e.g. cattle, sheep, goats, equines, swine, poultry, dogs or cats.

The compounds to animals infested by or exposed to infestation by arthropods, helminths or protozoa, by parenteral, oral or topical application of compositions in which the active ingredient exhibits an immediate and/or prolonged action over a period of time against the arthropods, helminths or protozoa, for example by incorporation in feed or suitable orally-ingestible pharmaceutical formulations, edible baits, salt licks, dietary supplements, pour-on formulations, sprays, baths, dips, showers, jets, dusts, greases, shampoos, creams, wax smears or livestock self-treatment systems.

Solid or liquid compositions for application topically to animals, timber, stored products or household goods usually contain from about 0.00005% to about 90%, more particularly from about 0.001% to about 10%, by weight of one or more compounds of formula (II) or veterinarily acceptable salts thereof. For administration to animals orally or parenterally, including percutaneously solid or liquid compositions, these normally contain from about 0.1% to about 90% by weight of one or more compounds of formula (II) or veterinarily acceptable salts thereof.

Medicated feedstuffs normally contain from about 0.001% to about 3% by weight of one or more compounds of formula (II) or veterinarily acceptable salts thereof. Concentrates or supplements for mixing with feedstuffs normally contain from about 5% to about 90%, preferably from about 5% to about 50%, by weight of one or more compounds of formula (II) or veterinarily acceptable salts thereof. Mineral salt licks normally contain from about 0.1% to about 10% by weight of one or more compounds of formula (II) or veterinarily acceptable salts thereof.

Dusts or liquid compositions for application to livestock, goods, premises or outdoor areas may contain from about 0.0001% to about 15%, more especially from about 0.005% to about 2.0%, by weight, of one or more compounds of formula (II) or veterinarily acceptable salts thereof. Suitable concentrations in treated waters are between about 0.0001 ppm and about 20 ppm, more particularly about 0.001 ppm to about 5.0 ppm. of one or more compounds of formula (II), or veterinarily acceptable salts thereof, and may be used therapeutically in fish farming with appropriate exposure times. Edible baits may contain from about 0.01% to about 5%, preferably from about 0.01% to about 1.0%, by weight, of one or more compounds of formula (II) or veterinarily acceptable salts thereof.

When administered to vertebrates parenterally, orally or by percutaneous or other means, the dosage of compounds of formula (II), or veterinarily acceptable salts thereof, will depend upon the species, age, or health of the vertebrate and upon the nature and degree of its actual or potential infestation by arthropod, helminth or protozoan pests. A single dose of about 0.1 to about 500, preferably from 0.1 to about 100 mg, preferably about 2.0 to about 20.0 mg, per kg body weight of the animal or doses of about 0.01 to about 20.0 mg, preferably about 0.1 to about 5.0 mg, per kg body weight of the animal per day, for sustained medication, are generally suitable by oral or parenteral administration. By use of sustained release formulations or devices, the daily doses required over a period of months may be combined and administered to animals on a single occasion.

The compounds of the invention may be administered most advantageously with another parasiticidally effective material, such as an endoparasiticide, and/or an

ectoparasiticide, and/or an endectoparasiticide. For example, such compounds include macrocyclic lactones such as avermectins or milbemycins e.g., ivermectin; pyratel (generally adminsitered as pyrantel pamoate) or an insect growth regulator such as lufenuron or methoprene.

By the term "parasites" as used in the specification and claims is meant endoparasites and ectoparasites of warm-blooded animals, particularly ectoparasites. Preferably, fleas and/or ticks are controlled by the method of the present invention.

Illustrative of specific parasites of various host animals which may be controlled by the methods of this invention include arthropods such as:

Mites: Mesostigmata spp. e.g. mesostigmatids such as the chicken mite, Dermanyssus gallinae; itch or scab mites such as Sarcoptidae spp. for example Sarcoptes scabiei; mange mites such as Psoroptidae spp. including Chorioptes bovis and Psoroptes ovis; chiggers e.g. Trombiculidae spp. for example the north american chigger, Trombicula alfreddugesi;

Ticks: e.g., soft-bodied ticks including Argasidae spp. for example Argas spp. and Ornithodoros spp ; hard-bodied ticks including Ixodidae spp., for example Rhipicephalus sanguineus, and Boophilus spp.;

Lice: sucking lice, e.g., Menopon spp. and Bovicola spp.; biting lice, e.g., Haematopinus spp., Linognathus spp. and Solenopotes spp.;

Fleas: e.g., Ctenocephalides spp., such as dog flea (Ctenocephalides canis) and cat flea (Ctenocephalides felis); Xenopsylla spp. such as oriental rat flea [Xenopsylla cheopis]; and Pulex spp. such as human flea [Pulex irritans];

True bugs: e.g., Cimicidae or including the common bed bug (Cimex lectularius);, Triatominae spp. including triatomid bugs also known as kissing bugs; for example Rhodnius prolixus and Triatoma spp.;

bloodsucking adult flies: (e.g., horn fly [Haematobia irritans], horse fly [Tabanus spp.], stable fly [Stomoxys calcitrans], black fly [Simulium spp.], deer fly [Chrysops spp.], louse fly [Melophagus ovinus], tsetse fly [Glossina spp.], mosquitoes [Culex spp., Anopheles spp., and Aedes spp.); and

parasitic fly maggots: (e.g., bot fly [Oestrus ovis and Cuterebra spp.], blow fly [Phaenicia spp.], screwworm [Cochliomyia hominivorax], cattle grub [Hypoderma spp.], fleeceworm.

The present invention also provides for the use of a compound of formula (I) or a salt thereof hereinbefore described as a therapeutic agent, preferably for animals, more preferably for domestic animals.

The veterinary composition may be sterile or non-sterile. It may be a liquid (e.g. aqueous) or solid (e.g., dry) composition, in particular a freeze-dried composition, which, by addition of water or another liquid, orally effective solutions may be prepared.

The present invention also provides for the use of a compound of formula (I) or a salt thereof as hereinbefore defined for the manufacture of a veterinary composition for the control of parasites in or on an animal.

In a further embodiment of the invention there is provided the use of a compound of formula (I) or salt thereof for controlling parasites in or on an animal without causing emesis of the animal.

Preferred is the use for orally administering the compound to the animal, which is preferably a domestic animal, highly preferred a cat or a dog.

In a further embodiment of the invention there is provided the use of a compound of formula (I) or salt thereof for the manufacture of a substantially non emetic composition, for controlling parasites in or on an animal, preferably for oral administering.

The present invention also relates to a method of cleaning animals in good health comprising the application to the animal of a compound of formula (I) or a salt thereof as hereinbefore defined to the animal.

The method of cleaning an animal is not a method of treatment by therapy of the animal body per se, because

(a) the animal is in good health and requires no substantial treatment to correct a deficiency of health;

(b) the cleaning of the animal is not intended to be done by veterinary personnel, but by persons interested in the cleaning of the animal; and

(c) the purpose of such cleaning is to avoid unpleasant conditions for humans and the environment in which humans inhabit so as to not infest the said humans with arthropods carried by the animal.

By "carrier" is meant an organic or inorganic material, which can be natural or synthetic, and which is associated with the compound and which facilitates its application to the animal. This carrier is thus generally inert and should be arthropocidally acceptable. The carrier can be solid (e.g., clay, silicates, silica, resins, wax.) or liquid (e.g., water, alcohols, ketones, oil solvents, polar aprotic solvents) An example of an oil solvent is corn oil. An example of a polar aprotic solvent is dimethyl sulfoxide.

The compounds of the invention also have utility in the control of arthropod or nematode pests of plants. The active compound is generally applied to the locus in which arthropod or nematode infestation is to be controlled at a rate of about 0.005 kg to about 25 kg of active compound per hectare of locus treated, preferably 0.02 to 2 kg/ha. Under ideal conditions, depending on the pest to be controlled, the lower rate may offer adequate protection. On the other hand, adverse weather conditions, resistance of the pest and other factors may require that the active ingredient be used in higher proportions. For foliar application, a rate of 0.01 to 1 kg/ha may be used.

When the pest is soil-borne, the formulation containing the active compound is distributed evenly over the area to be treated in any convenient manner. Application may be made, if desired, to the field or crop-growing area generally or in close proximity to the seed or plant to be protected from attack. The active component can be washed into the soil by spraying with water over the area or can be left to the natural action of rainfall. During or after application, the formulation can, if desired, be distributed mechanically in the soil, for example by ploughing or disking.

Application can be prior to planting, at planting, after planting but before sprouting has taken place or after sprouting.

The compounds of the invention may be applied in solid or liquid compositions to the soil principally to control those nematodes dwelling therein but also to the foliage principally to control those nematodes attacking the aerial parts of the plants (e.g. aphelenchoides spp. and ditylenchus spp. listed above).

The compounds of the invention are of value in controlling pests which feed on parts of the plant remote from the point of application, e.g. leaf feeding insects are killed by the subject compounds applied to roots. In addition the compounds may reduce attacks on the plant by means of antifeeding or repellent effects.

The compounds of the invention are of particular value in the protection of field, forage, plantation, glasshouse, orchard and vineyard crops, or ornamentals and of plantation and forest trees, for example, cereals (such as maize, wheat, rice, sorghum), cotton, tobacco, vegetables and salads (such as beans, cole crops, curcurbits, lettuce, onions, tomatoes and peppers), field crops (such as potato, sugar beet, ground nuts, soyabean, oil seed rape), sugar cane, grassland and forage (such as maize, sorghum, lucerne), plantations (such as of tea, coffee, cocoa, banana, oil palm, coconut, rubber, spices), orchards and groves (such as of stone and pip fruit, citrus, kiwifruit, avocado, mango, olives, and walnuts), vineyards, ornamental plants, flowers and shrubs under glass and in gardens and parks, forest trees (both deciduous and evergreen) in forests, plantations and nurseries.

They are also valuable in the protection of timber (standing, felled, converted, stored or structural) from attack by sawflies (e.g. urocerus) or beetles (e.g. scolytids, platypodids, lyctids, bostrychids, cerambycids, anobiids), or termites, for example, reticulitermes spp., heterotermes spp., coptotermes.

They have applications in the protection of stored products such as grains, fruits, nuts, spices and tobacco, whether whole, milled or compounded into products, from moth, beetle and mite attack. Also protected are stored animal products such as skins, hair, wool and feathers in natural or converted form (e.g. as carpets or textiles) from moth and beetle attack; also stored meat and fish from beetle, mite and fly attack.

The disclosure in US provisional application No. 60/168658 from which this application claims priority is incorporated herein by reference.

The invention is further illustrated by the following examples, without limiting it thereto.

Examples and Preparations

Example 1

Preparation of 1-(2,6-Dichloro-4-trifluoromethylphenyl)- 3-cyano-4-trifluoromethylsulfinyl-5-hydroxypyrazole. To a solution of 15 g (35.5 mmol) of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-hydroxypyrazole in 125 ml of dichloromethane at room temperature was added a solution of m-chloroperbenzoic acid (8.76 g, 70 %, 35.5 mmol) in 375 ml of dichloromehane. The resulting solution was stirred at room temperature for 17 hr. It was then concentrated and triturated with ethyl acetate and heptane(1:2). Upon filtration a solid was obtained. This solid was dissolved in ethyl acetate and stirred with saturated sodium bicarbonate solution. Ther layers were separated and the aqueous layer was extracted with three times of ethyl acetate. The combined organic layer was dried (magnesium sulfate) and concentrated. Upon chromatographic purification via silica gel column, a solid (5.7 g, 13.01 mol, 37 %) was obtained as the desired product, mp 185-187d.

Example 2

Preparation of 1-(2,6-Dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfonyl-5-hydroxypyrazole. To the solution of 2 g (4.74 mmol) of 1-(2,6-dichloro-4trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-

hydroxypyrazole in 1,2-dichloroethane was added 1.83 ml (9.52 mmol, 35 % in acetic acid) of peracetic acid at room temperature. The resulting solution was heated up to 60 C for 9 hr. It was then cooled and concentrated to give 2.05 g of residue. Upon chromatographic purification via silica gel column eluting with gradient solvent mixture (heptance/ethyl acetate), an oil (1.08 g, 2.38 mmol, 50.2 % yield) was obtained as the desired product with 98 % HPLC puriety; F-NMR, -60.999 ppm (AR-CF3), -79.893 ppm (SO2CF3). H-NMR, 8.18 ppm (s, 2 H).

Example 3

Preparation of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-amido-4-trifluoromethylsulfenyl-5-hydroxypyrazole. To the mixture of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-hydroxypyrazole (3.0 g, 7.13 mmol) and concentrated sulfuric acid (3 ml) was heated at 100 C for 3 hr. The reaction mixture was cooled and poured into ice-water. A solid was collected via filtration and was washed with water. It was then vacuum dried to obtain a solid (2.88 g, 6.56 mmol, 92 % yield) with 98 % HPLC puriety, m. p. 197-198 C.

Example 4

Preparation of 1-(2,6-dichloro4-trifluoromethylphenyl)-3-thioamido-4-trifluoromethylsulfenyl-5-hydroxypyrazole. To the mixture of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-amido-4-trifluoromethylsulfenyl-5-hydroxypyrazole (1 g, 2.28 mmol) and Lawesson's reagent (0.49 g, 1.21 mmol) in toluene was heated up to reflux for 4 hr. The reaction mixture turned into a solution during this time. This solution was then cooled , concentrated, and via chromatographic purification to provide a solid (0.283 g, 0.623 mmol, 27.3 % yield) with 96 % HPLC puriety m. p. 150--151 decomp.

Example 5

Preparation of 1-(2,6-Dichloro-4-trifluoromethylphenyl)-3-oximicamido-4-trifluoromethylsulfenyl-5-hydroxypyrazole. To the solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-hydroxypyrazole (3.0 g, 7.11 mmol) in 15 ml of methanol at room temperature was added hydroxyamine hydrochloride (0.59 g, 8.53 mmol) and triethylamine (0.94 g, 9.24 mmol). The resulting mixture was stirred at room temperature for a total of 48 hr with additional hydroxyamine hydrochloride (1.18g, 17.06 mmol) and triethylamine (1.88 g, 18.5 mmol) added portionwise. The resulting reaction mixture was concentrated and then dissolved in ethyl acetate. The organic layer was washed with saturated ammonium chloride, water,dried (sodium sulfate), concentrated to give a brown oil which solidified after standing, m. p. 184 C.

Example 6

Preparation of 1-(2,6-Dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-trimethylacetoxypyrazole. To the solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-hydroxypyrazole (7.00 g, 16.6 mmol) and pyridine (4.91 g, 62.1 mmol) in 1,2-dichloroethane at room temperature was added trimethylacetyl chloride (4.37 g, 36.2 mmol) dropwise. Ice bath was used to maintain the temperature of the reaction. After 20 hr at room temperature, the orgainc layer was washed with five times of aqueous KHSO4 till the aqueous solution was at pH 1. The orgainc layer was then dried (Mg SO4) and concentrated to give a solid residue. Upon chromatographic purification via silica gel column of the solid residue, after trituration with pentane, a off white solid (2.403 g, 28.6 % yield, 97.0 % HPLC puriety) was provided as the desired product, m. p. 82-83 C.

Example 7

Preparation of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-chlorodifluoromethylsulfenyl-5-hydroxypyrazole. To the solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-5-hydroxypyrazole (12.0 g, 37.3 mmol.) and pyridine (3.25 g, 41.0 mmol) in dichloromethane at -50– -60 C was added chlorodifluoromethanesulfenyl chloride (8.1 g, 46.6 mmol). The resulting solution was gradually warmed up to room temperature. After 20 hr, the organic layer was washed five times with water. It was then washed with brine and dried (Na2SO4) to provide an oil. Upon chromatographic purification of the oil , a total of 11.6 g (26.4 mmol., 71 % yield) of the desired product with 97 % HPLC puriety was isolated. F-NMR: -30.05 ppm (CClF2), -63.80 ppm (ArCF3).

Biological Example

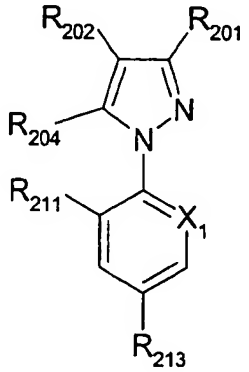
The compounds 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylthio-5-hydroxypyrazole, 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfinyl-5-hydroxypyrazole and 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfonyl-5-hydroxypyrazole are formulated as a 30 mg/mL formulations in a 1:1 volume/volume solution of dimethyl sulfoxide and corn oil. Using this formulation, mixed breed dogs and cats are treated at a rate of 10 mg of the compound per kg (mg/kg)of body weight of the dog and 20 mg/kg of the cat treated. The animals are fasted for at least 8 hours prior to treatment, fed half of the daily ration immediately prior to treatment, then allowed access to the remainder of the daily ration immediately following treatment.

All dogs are infested with cat fleas (Ctenocephalides felis) and with ticks (Rhipicephalus sanguineus) 1 day prior to administration of the compound. Cats are only infested with fleas. The initial flea and tick counts are performed 1 day after the administration of the compounds. At 7, 14, 21 and 28 days after treatment the dogs

are re-infested with ticks and 8, 15, 22 and 29 days after treatment the dogs and cats are re-infested with fleas. At 1, 9, 16, 23 and 30 days after treatment the control of fleas and ticks in treated dogs and cats is determined versus a group of infested dogs and cats which receive a placebo consisting of a 1:1 volume/volume solution of dimethyl sulfoxide and corn oil. To determine the efficacies of the compounds, the arthropods are combed from the animals and counted. Satisfactory results are obtained for many of the above-mentioned compounds in any of the three areas of evaluation without any significant side effect for a period ranging from eight to thirty days: control of flea on dog, control of tick on dog, and control of flea on cat. They are: 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-trimethylacetoxypyrazole 3-10 , 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-ethoxypyrazole 3-1, 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-chlorodifluoromethylsulfenyl-5-hydroxypyrazole 1-9 , 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfenyl-5-hydroxypyrazole 1-1 , 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfonyl-5-hydroxypyrazole 1-5, 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylsulfinyl-5-hydroxypyrazole 1-3 , 1-(2,6-dichloro-4-trifluormethyl(phenyl)-3-cyano-4-trifluormethylsulfonyl-5-N,N-dimethylcarbamyloxypyrazole 19-1.

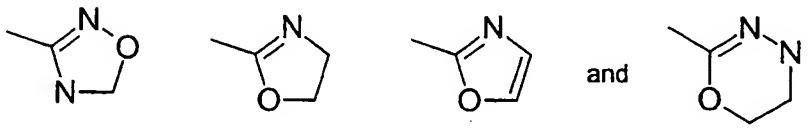
CLAIMS

1. A method of controlling parasites in or on an animal comprising administering to the animal a parasiticidally effective, substantially non-emetic amount of a 1-arylpyrazole of formula (I):



wherein:

R_{201} is cyano, C(O)alkyl, $C(S)NH_2$, $C(NH)OR_{203}$, $C(NH)SR_{203}$, alkyl, $C(=NOH)NH_2$, $C(=NNH_2)NH_2$, $C(O)NH_2$, $C(O)NHR_{205}$, $C(O)NR_{205}R_{206}$, haloalkyl or heterocyclyl from the group:



optionally substituted by R_{203};

R_{202} is $S(O)_hR_{203}$, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, cycloalkyl, halocycloalkyl, cycloalkyl-alkyl , C_2-C_6 alkynyl, nitro or imidazol-2-yl optionally substituted by alkyl, alkoxy, haloalkyl, halogen, cyano and/or nitro;

R_{203} is alkyl or haloalkyl;

R_{204} is -OH, $R_{205}O$-, HC(O)O-, $R_{205}C(O)O$-, $R_{205}OC(O)O$-, $NH_2C(O)O$-, $R_{205}NHC(O)O$-, $R_{205}R_{206}NC(O)O$-, $R_{205}S(O)_nC(O)O$-, $R_{206}SO_2O$-, aryl-SO_2O-, (C_4-C_7)-oxacycloalkyloxy,

$R_{205}R_{206}N$-C(NR_{205})-O-, $R_{205}R_{206}N$-C(NH)-O- , $R_{205}NH$-C(NR_{205})-O-, $R_{205}NH$-C(NH)-O-, $R_{205}N$=CH-O-, $R_{205}N$=C(R_{206})-O-, $R_{205}NH$-C(S)-O-, $R_{205}R_{206}N$-C(S)-O- ;

R_{205} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, adamantyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, haloalkylaminoalkyl, di(haloalkyl)aminoalkyl, aryl optionally substituted, hetaryl optionally substituted, arylalkyl optionally substituted, hetarylalkyl optionally substituted, C_2-C_6 alkenyl, C_2-C_6 alkinyl;

R_{206} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, aryl optionally substituted, hetaryl optionally substituted, arylalkyl optionally substituted, hetarylalkyl optionally substituted;

or R_{205} and R_{206} may form together with the nitrogen to which they are attached a 3 to 7 membered ring which additionally may contain one or more heteroatoms selected from nitrogen, oxygen and sulfur;

X_1 is selected from nitrogen and C-R_{212};

R_{211}, R_{212} are independently selected from halogen, hydrogen, CN, C_1-C_3 alkyl and NO_2;

R_{213} is selected from halogen, haloalkyl, haloalkoxy, -$S(O)_kCF_3$, and $-SF_5$ or forms a ring with R_{214};

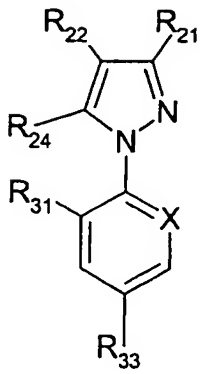
R_{214} is hydrogen or may constitute together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring;

and

h, k and n are independently selected from 0, 1, and 2;

and veterinarily acceptable salts thereof.

2. A method of controlling parasites in or on an animal as claimed in claim 1 by administering to the animal an 1-arylpyrazole of formula (II):



(II)

wherein:

R_{21} is cyano, $C(=S)NH_2$, $C(=NOH)NH_2$ or $C(=NNH_2)NH_2$;

R_{22} is $S(O)_mR_{23}$;

R_{23} is alkyl or haloalkyl;

R_{24} is OH, HC(O)O-, $R_{25}C(O)O$-, $R_{25}OC(O)O$- or $R_{25}S(O)_nC(O)O$-

R_{25} is alkyl, haloalkyl, cycloalkyl, halocycloalkyl, alkoxyalkyl, haloalkoxyalkyl, adamantyl, adamantyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, haloalkylaminoalkyl, di(haloalkyl)aminoalkyl, aryl optionally substituted, hetaryl optionally substituted, arylalkyl optionally substituted, hetarylalkyl optionally substituted, C_2-C_6 alkenyl, C_2-C_6 alkinyl,

or two groups R_{25} may form together with the nitrogen to which they are attached a 3 to 7 membered ring which additionally may contain one or more heteroatoms selected from nitrogen, oxygen and sulfur;

X is selected from nitrogen and C-R_{32};

R_{31} and R_{32} are independently selected from halogen, hydrogen, CN, C_1-C_3 alkyl and NO_2;

R_{33} is selected from halogen, haloalkyl, haloalkoxy, $-S(O)_rCF_3$, and $-SF_5$ or forms a ring together with R_{34} ;

R_{34} is hydrogen or may constitute together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring;

m is 0, 1 or 2;

r is selected from 0, 1, and 2;

and veterinarily acceptable salts thereof; provided that if R_{21} is cyano then R_{24} is not $R_{25}R_{25}$-N-C(O)-O-.

3. A compound of formula (II) or salt there of as hereinbefore described in claim 2 with the proviso that the compound is not 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluoromethylthio-5-hydroxypyrazole.

4. A compound according to claim 3 wherein

R_{21} is cyano;

R_{22} is $S(O)_mR_{23}$;

R_{23} is haloalkyl, preferably CF_3;

R_{24} is OH;

X is selected from nitrogen and C-R_{32};

R_{31} and R_{32} are independently selected from halogen,

R_{33} is selected from halogen, haloalkyl, haloalkoxy, -$S(O)_rCF_3$, and $-SF_5$;

m and r are independently selected from 0, 1, and 2.

5. The compound of formula (I) as defined in Claim 1 or the compound of formula (II) as defined in any one of claims 2,3 or 4 which is 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfinyl-5-hydroxypyrazole.

6. The compound of formula (I) as defined in Claim 1 or the compound of formula (II) as defined in any one of claims 2,3 or 4 which is 1-(2,6-dichloro-4-trifluoromethylphenyl)-3-cyano-4-trifluromethylsulfonyl-5-hydroxypyrazole.

7. A composition comprising a parasiticidally effective, amount of a compound of formula (I) or (II) or a salt thereof as defined in any one of the foregoing claims and an acceptable carrier.

8. A composition comprising a parasiticidally effective, amount of a compound of formula (II) or a salt thereof and an acceptable carrier as defined in any one of claims 2, 3, 4, 5 or 6.

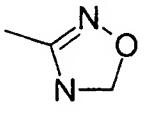
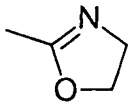
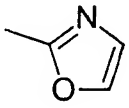
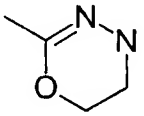
9. The method according to claims 1 wherein the animal is a domestic animal.

10. The method according to claim 1 wherein the 1-arylpyrazole is administered orally in a dose to the animal in a dose range from 0.1 to 500 mg/kg.

11. A compound of formula (I) according to claim 1

wherein

R_{201} is cyano, C(O)alkyl, $C(S)NH_2$, $C(NH)OR_{203}$, $C(NH)SR_{203}$, alkyl, $C(=NOH)NH_2$, $C(=NNH_2)NH_2$, $C(O)NH_2$, $C(O)NHR_{205}$; $C(O)NR_{205}R_{206}$, haloalkyl or heterocyclyl from the group:




and


optionally substituted by R_{203};

and/or

R_{202} is $S(O)_nR_{203}$, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, cycloalkyl, halocycloalkyl, cycloalkyl-alkyl , C_2-C_6 alkynyl, nitro or imidazol-2-yl optionally substituted by alkyl, alkoxy, haloalkyl, halogen, cyano and/or nitro;

and/or

R_{204} is -OH, $R_{205}O$-, HC(O)O-, $R_{205}C(O)O$-, $R_{205}OC(O)O$-, $NH_2C(O)O$-, $R_{205}NHC(O)O$-, $R_{205}R_{206}NC(O)O$-, $R_{205}S(O)_nC(O)O$-, $R_{206}SO_2O$-, aryl-SO_2O-, (C_4-C_7)-oxacycloalkyloxy, $R_{205}R_{206}N$-C(NR_{205})-O-, $R_{205}R_{206}N$-C(NH)-O- , $R_{205}NH$-C(NR_{205})-O-, $R_{205}NH$-C(NH)-O-, $R_{205}N$=CH-O-, $R_{205}N$=C(R_{206})-O-, $R_{205}NH$-C(S)-O-, $R_{205}R_{206}N$-C(S)-O- ;

and/or

R_{214} constitutes together with R_{213} a group of OCF_2O, CF_2OCF_2, CF_2OCF_2O and CF_2CF_2O, which forms together with the carbons they are attached to a five to six membered ring;

12. The use of a compound of formula (I) according to claim 1 for controlling parasites in animals.